THE PYROLYSIS OF N-BUTANE

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ABSTRACT.

A study of the pyrolysis of n-butane was carried out using an all-gold tubular reactor. The initial rate of decomposition of the n-butane was of 1.50-order with respect to the partial pressure of the n-butane. A free radical mechanism, similar to that originally proposed by Rice, accounted satisfactorily for the distribution of products. Oxygen was rigorously excluded from the pyrolysis gases. The surfaces of the gold reactor had been acid-treated to remove oxide impurities.

Some preliminary experiments were performed in the partial oxidation of n-butane.

SUMMARY.

A study of the pyrolysis of n-butane was carried out using an all-gold tubular reactor. Products of the pyrolysis were analysed by gas chromatography. The pyrolytic decomposition was carried out under the following conditions:

Temperature: 529 to 595°C.

Total pressure: 5 to 20 psia.

Mole fraction of butane: 0.025 to 0.98 with various inert diluents.

Mean contact time: 0.55 to 4.0 sec.

Conversion of n-butane: less than 2%

Trace level of oxygen: less than 2 ppm.

In that region of the pyrolysis where the kinetics could be described by an order of 1.50 with respect to the pressure of n-butane, the rate constant for the decomposition was given by:

$$k = 2.27 \times 10^{17} \exp(-66{,}000/RT) \quad ml.^{\frac{1}{2}} \, mole^{-\frac{1}{2}} \, sec.^{-1}$$

This expression correlated data taken on an all-gold tubular reactor operated under conditions of laminar flow. The reactor was treated as being an isothermal, plug-flow unit. Surface impurities in the gold had been removed by acid treatment. A free radical mechanism, similar to that

originally proposed by Rice, accounted satisfactorily for the distribution of products.

With an excess of diluent in the system (mole fraction of n-butane less than 0.3) the rate of reaction was increased over that predicted by the above expression. The increase in rate was directly related to the pressure of inert gas. It was not possible to pinpoint unambiguously the cause of the increase in the rate of reaction though several hypotheses were developed to account for the phenomenon.

Comparison of the results of this study with data taken on the decomposition in quartz and pyrex reactors showed satisfactory agreement; this was taken as indicating that the gold surfaces were relatively inert. The pyrolysis was, however, markedly influenced by the presence of impurities on the gold surfaces. The exact nature of these impurities was not determined though the oxides of copper and iron were probable components.

Trace amounts of oxygen were shown to markedly influence the formation of butenes and to exert a mildly inhibitory effect on the formation of cracked products. With higher levels of oxygen, butenes were among the initial products of reaction but were rapidly attacked further by oxygen.

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INTRODUCTION.

The Thermal Decomposition of Hydrocarbons.

The thermal decompositions of paraffinic hydrocarbons have been the subject of considerable experimental study. Early workers (3) soon realised that the large number of products resulting from the thermal decomposition of a single organic species suggested a complex reaction system. The rationale for studying a complex reaction system was usually given in terms of understanding the free radical reactions which account for the major part of the decomposition process. The commercial impetus for an understanding of pyrolytic decomposition stems from the widespread use of the products of decomposition as petrochemical intermediaries (1,2). Despite the extent of these investigations agreement amongst the results has been rare. The mechanism of decomposition is extremely complex due to the large number of free radical reactions which are possible under pyrolysis conditions, and also to the ease with which these reactions can be affected by the presence of trace impurities and spurious surface effects.

Rice (3) was the first worker to consider the free radical nature of pyrolytic systems. He postulated initiation by a C-C bond cleavage to form free radicals and subsequent chain processes involving reactions of the free

radicals with the original hydrocarbon. The basic tenets of Rice's theory may be summarised as:

i) Initiation: Free radicals are generated by the splitting of the molecule at its weakest link.

ii) Chain propagation: A radical may abstract a H atom from the parent molecule to form a small saturated molecule and a new free radical. The attacking radical is designated a β radical. Alternatively, a free radical may undergo a unimolecular decomposition to form an olefin, the radical being called a μ radical.

iii) Chain termination: This occurs through association or disproportionation of β or μ radicals.

With some approximations the mechanisms proposed by Rice have been able to explain the fact that many complex decompositions have simple orders of 1.0, 1.5, or 2.0 (4). The composition of the product was determined mainly by the chain cycle, the initiation and termination processes affecting the overall kinetics. Furthermore, the overall activation energy for the decomposition was much less than the C-C bond energy. Subsequent work has strengthened the basic premises of the Rice theory and most interpretations of complex decompositions are based within its framework. Although the Rice mechanism gives a satisfactory prediction of the product distribution it is not so effective in

explaining some of the kinetic features of decomposition processes, (5).

Within the homologous series of paraffinic hydrocarbons, pyrolysis studies have ranged from methane (6,7) to hexadecane (8,53). Ethane in particular has been widely studied (9). The reasons for the present study of n-butane are:

i) There are considerable discrepancies among the available data (10), and there has been little work done at pressures above one atmosphere.

ii) Butane decomposes at a measurable rate at suitable temperatures, and the metering of flow of butane presents no special problems. These experimental simplifications do not hold for the other members of the paraffin series.

iii) The decomposition of n-butane takes place by a mechanism which involves mainly alkyl radicals. Hydrogen atoms are the main chain carriers in the decomposition of simpler paraffins but they play a minimal role in the pyrolysis of n-butane. Heterogeneous reactions can become more significant when hydrogen atoms are the main chain carriers (54).

The Pyrolysis of n-Butane.

Early investigations into the pyrolysis of n-butane

were carried out by Pease and Durgen (11) using a flow reactor operated at 1 atm. pressure and 600 to 650°C. They concluded that the decomposition was mainly homogeneous and had first-order behavior with an activation energy of 65 kcal. The first-order rate constant decreased with increasing extent of reaction, and this effect was attributed to secondary reactions. Steacie and Puddington (24) used a static method at temperatures of 510 to 570°C. and pressures between 5 and 60 cm. mercury. They also found a fall-off in the first-order rate constant. Of even greater interest was the fact that the product distribution showed only small changes with variations in temperature, pressure and extent of decomposition.

In these and other early experimental studies (12,13) the extent of the decomposition of butane usually exceeded 20%. To identify the initial products the product distributions should be extrapolated to their values at zero conversion. Crawford and Steacie (14) investigated the reaction at 440°C. in the pressure range 4 to 13 cm.. The rates of formation of the major products were found to be constant from 1.5 to 9.0% conversion. With decompositions in excess of 10% marked decreases in the rate of reaction were noted. On the other hand, the relative amounts of each product remained constant upto 24% decomposition which, they claimed, implied that no secondary reactions occurred.

Other workers have been aware of the possibility of secondary reactions. Nehaus and Marek (15) operated a reactor at 600 to 650°C. and 1 atm. pressure. They concluded that propane was a secondary product and that no butadiene was formed at these temperatures. More recently, Sandler and Chung (16) noted objections (17) that measurements of reaction rates in many systems were governed by heat-transfer phenomena. They also noted that with high degrees of conversion there may be some differences in the apparent overall activation energies as determined by static and flow experiments, due to the differing heat-transfer effects. As a result of the improved heat-transfer the reaction in an annular reactor was found to be significantly faster than that in a tubular reactor.

In a series of papers, (18,19,20,54), Purnell and Quinn have described their studies of the pyrolysis in the temperature range 420 to 530°C. and a pressure range of 10 to 150 mm. using a static reactor. Particular care was taken with regard to working with reproducible surfaces; the reaction was studied in a pyrex vessel which had been cleaned with nitric acid. The decomposition was considered to be essentially homogeneous. The major products of the decomposition were hydrogen, methane, ethane, ethylene and propylene. No propane was formed in the initial stages of the pyrolysis, however traces of butenes and higher

products were formed at higher conversion levels. They also noted:

i) There was no induction period for formation of the major products.

ii) The distribution of major products was independent of the conversion at any given initial temperature and pressure.

iii) The yields of propylene and methane were identical.

iv) The yield of hydrogen was determined by the difference in the yields of ethylene and ethane.

The important role of the ethyl radical in determining the kinetic features of the pyrolysis was outlined (19); the unimolecular decomposition of the ethyl radical was thought to be in its pressure dependent region. The following scheme, incorporating the principles proposed by Rice, gave a good interpretation of the experimental evidence:

Initiation:

$$C_4H_{10} \longrightarrow 2\ C_2H_5^{\bullet}$$

$$C_4H_{10} \longrightarrow CH_3^{\bullet} + C_3H_7^{\bullet}$$

Propagation:

$$C_2H_5^{\bullet} + C_4H_{10} \longrightarrow C_2H_6 + C_4H_9^{\bullet}$$

$$CH_3^{\bullet} + C_4H_{10} \longrightarrow CH_4 + C_4H_9^{\bullet}$$

$$C_4H_9^{\bullet} \longrightarrow C_2H_4 + C_2H_5^{\bullet}$$

$$C_4H_9^{\bullet} \longrightarrow C_3H_6 + CH_3^{\bullet}$$

$$C_2H_5^{\bullet} \longrightarrow C_2H_4 + H^{\bullet}$$

$$H^{\bullet} + C_4H_{10} \longrightarrow C_4H_9^{\bullet} + H_2$$

Termination: $2\ C_2H_5^{\cdot} \longrightarrow C_4H_{10}$

and $2\ C_2H_5^{\cdot} \longrightarrow C_2H_4 + C_2H_6$

A long chain length was proposed to account for the fact that the proportion of C_2 hydrocarbons was not dependent on the pressure, and also the fact that propane and butenes were not generated in the early stages of the reaction. The variation of the overall activation energy with pressure reflected the fact that the ethyl radical (a chain center) could propagate the chain by competing reactions of different orders and activation energies.

Laidler and his co-workers (21,22) have studied the kinetics of the pyrolysis of n-butane in a batch reactor at temperatures from 520 to 590°C. and at pressures from 30 to 600 mm.. The rate of decomposition of butane was found to be accurately 1.50-order and the overall activation energy was 59.9 kcal./mole. An induction period of several seconds duration was noticed. The decomposition was sensitive to the state of the surface; packing the vessel with quartz and conditioning it usually led to a decrease in the rate of reaction. They concluded that the pyrolysis was largely homogeneous and that the surface effect could be attributed to surface catalysis of the recombination of ethyl radicals. They proposed an overall reaction scheme which was similar to that due to Purnell and Quinn.

Benson (9,23) proposed a two-chain mechanism to

explain the product distributions reported by Steacie (24). One chain was presumed to be due to the n-butyl radical and led to ethane and ethylene. The other was considered to be due to the sec-butyl radical and led to methane and propylene. The fact that bond strengths of secondary hydrogen atoms were less than those of primary hydrogen atoms implied that sec-butyl radicals would lead to the observed preponderance of methane and propylene. Other workers have confirmed the estimate that sec-butyl radicals are formed more easily (25,26). Benson also drew attention to the problem of the correct assignement of the pressure dependence of the unimolecular step in pyrolytic chains. His proposed mechanism was basically very similar to that of Purnell and Quinn, even though the latter did not find it necessary to distinguish between n- and sec- radicals.

Wang and his co-workers studied the decomposition of n-butane in a one inch diameter tubular ceramic reactor (10,27). A temperature range of 460 to 560°C. was covered, the reactor being held at atmospheric pressure. With low conversion levels an accurate estimation of the initial rate of decomposition was possible and secondary reactions were negligible. The product distribution was found to be in good agreement with the results of Purnell and Quinn (19). The energy, momentum and mass transport were considered in an account of the reactor system. Temperature and composition profiles were determined and were used to

justify the treatment of the reactor as an isothermal, plug-flow unit. The data could be correlated equally well by both first- and second-order kinetics. The overall activation energy for the first-order rate constant was 54.6 kcal./mole. An exhaustive set of free-radical reactions was included into a Rice-type mechanism.

In addition to the conventional methods of study, three other experimental techniques should be briefly noted. Some use of the shock tube has been made in pyrolysis work (56,57,67). Evidently at very high temperatures (1000 to 1400°C.) the formation of several additional species is possible (56). The interpretation of data from shock tube studies is by no means as direct as that from conventional studies. A new technique which shows promise is that of low-pressure pyrolysis in which a gas is pyrolysed under conditions where gas-wall collisions predominate (58); product analysis is necessarily by mass spectrometry. The third development is due Whitten and Rabinovitch (59) wherein, by the addition of methylene radicals to propane, chemically activated butane (both n- and iso-) was formed; the butane would decompose at room temperature. The primary aim of this method was to deduce information on the uni-molecular decomposition of the parent molecule. Although the use of a low temperature reduced the possibility of secondary abstraction reactions, the reaction scheme was much more complex than that required to describe the

conventional pyrolysis.

The Effects of Added Gases.

Hinshelwood and Stavely (28) first noted that nitric oxide inhibited the decomposition of paraffins and asserted that the effect was due to the ability of the nitric oxide to react with, and remove, the chain carrying radicals. The inhibition effect is often used as a diagnostic test for a free radical reaction; later work has confirmed that several other materials will act as inhibitors. There has been much controversy concerning the nature of the "residual" reaction of the paraffin in an excess of inhibitor. The limiting rate was thought to be independent of the inhibitor used (29), and the products from the normal and inhibited pyrolyses were very similar. Experimental work on the isotopic mixing that can occur when a deuterated compound is decomposed in the presence of a paraffin has shown that amounts of deuterated products formed were the same for both inhibited and uninhibited reactions; this is considered to be strong evidence for some free radical participation in the fully inhibited reaction (25,5). A recent review by Gowenlock (30) concluded that the inhibited reaction has mainly free radical characteristics and that the nitric oxide could have a dual initiation-termination role. Back and Laidler (31) contended that it was necessary to postulate hydrogen

abstraction by the nitric oxide and that surface reactions were involved.

Propylene has also been used as a free radical scavenger (32,60). As noted by both Gowenlock and Quinn (30,60) propylene can exert a considerable kinetic role due to the formation of new chain centers. Quinn (60) found that the addition of propylene resulted in increased yields of higher products (butenes) and also the formation of one product (1-pentene) which was not formed in the initial stages of the pyrolysis of either pure reactant. Quinn interpreted his observations in terms of a co-pyrolysis scheme involving two mutually interacting chain systems.

Early work by Pease and Durgen (11) noted that the addition of nitrogen diluent gas (to 50% molar concentration) increased the rate slightly and that more hydrogen was formed. Purnell found that ethylene was formed at the expense of ethane when carbon dioxide was added to the pyrolysis gas (19). Other workers (22,25) reported that the addition of carbon dioxide had a negligible effect on the rate of decomposition. Rice (33) has remarked that the effects of inert gases and of surfaces may be inter-related in some systems, and that their study should prove to be an interesting diagnostic tool.

The Molecular Versus Chain Controversy.

The relative importance of free radical and molecular

processes in the pyrolyses of hydrocarbons has been the subject of considerable controversy. The original evidence favoring some molecular decomposition was presented in terms of the limiting inhibition effect produced by adding an excess of inhibitor, such as nitric oxide or propylene, to the reaction system.(28,29). In the light of recent experimental evidence from the isotope exchange studies of Kupperman and Larson (25), the mass spectrometric studies of Eltenton (49), and the detailed analytical studies of Purnell and Quinn (18,19) it is now considered to be well established that the thermal decomposition of n-butane is an entirely free radical process. Whitten and Rabinovitch (59) showed that only a trace amount of molecular decomposition was possible from chemically activated butane which had been formed by the addition of methylene radicals to propylene.

Surface Effects in the Pyrolysis of n-Butane

The severe temperatures used in pyrolysis studies (400 to 700°C.) have restricted the number of suitable construction materials. The only materials which have hitherto proved useful for pyrolytic studies are borosilicate glasses, ceramic materials, quartz, and stainless steel.

Kondrat'ev (35b) has noted that the formation of a radical at a surface can be thermodynamically more

advantageous than the gas-phase dissociation of the molecule into free radicals. Considering the dissociation:

$$RR' + K \longrightarrow R + R'K \qquad (K \text{ is a surface site})$$

this process gives an energy gain (equal to the energy liberated in the formation of the exothermic compound R'K) compared with the process:

$$RR' \longrightarrow R + R'$$

At higher temperatures the homogeneous process will be favored (6).

Early studies, which were carried to high decompositions, showed that the pyrolyses were frequently not-reproducible in clean, new vessels but achieved stability when the surfaces were coated with a carbonaceous deposit, after which the rates of decomposition appeared to be independent of the surface-to-volume ratio (11,14). Rice and Herzfeld interpreted this type of behavior as indicating both the initiation and termination of chains at the wall (33). Although early workers presumed the absence of marked surface effects to indicate a truly homogeneous reaction (34) more recent studies have shown the presence of some wall effects (16,18,22) and confirmed the premises of Rice and Herzfeld.

By examining the influence of various pre-treatments of pyrex vessels, Purnell and Quinn (18) concluded that clean surfaces did not affect the pyrolysis but that a heterogeneous chain termination could occur in carbon

conditioned vessels. Other studies have shown slight inhibition effects in quartz (22) and Vycor (16) vessels. The extent of the inhibition in a quartz system was sensitive to the state of the surface; any change from a clean, unpacked vessel raised the overall activation energy of the decomposition (22). Laidler suggested that free surface sites on the quartz could abstract hydrogen atoms from the butane molecule; he also noted that a conditioned surface was a better inhibitor than initiator. In contrast, Niclause et al (36) found that in both quartz and pyrex vessels the initial rates of decomposition of isopentane and propane were independent of the surface-to-volume ratio. A small amount of contamination by oxygen was found to significantly affect the influence of the surface-to-volume ratio (36) and was suggested as a basis for explaining some of the inconsistencies in earlier work (5).

The catalytic activity of 18/8 stainless-steel on paraffinic decomposition has been studied by Shabtai (37) who concluded the main effect to be a catalytic hydrogenation on the surface of the steel. It further appeared that the catalytic activity resulted from traces of chromic oxide in the surface layer, the steel surfaces being relatively non-catalytic. Sandler and Chung (16) studied the characteristics of several reactor tubes prepared from silica, Vycor, porcelain and a chrome-plated steel tube.

The Vycor tube was considered to be relatively inert.

The formation of carbon in a pyrolytic system is a complex phenomenon involving several distinct processes, depending on the temperature (51). In some systems there is both surface formation of carbon and soot formation in the gas phase. The most detailed study of carbon formation is due to Cullis et al (51) who studied the role of acetylenic hydrocarbons in the formation of carbonaceous deposits. Rao et al (57), from shock tube experiments, proposed that carbon formation in the pyrolysis of methane and ethane was probably due to the reaction of C_2 radicals with an acetylenic intermediate. Some of the early shock tube studies on soot formation at high temperatures were reviewed by Gaydon and Hurle (66). One worker has shown that the carbonaceous deposits resulting from the decomposition of some organic species have significant concentrations of free radicals (52).

Influence of Trace Amounts of Oxygen on the Pyrolysis.

Kondrat'ev (35a) has noted that the reaction:

$$RH + O_2 \longrightarrow R^{\cdot} + HO_2^{\cdot}$$

can be considered a general mechanism of radical formation involving oxygen. The activation energy of this process differs little from its heat of reaction which is estimated as 40 to 50 kcal/mole. Therefore, the rate of the above reaction is usually much greater than that of any reaction

involving a simple dissociation of the molecule, which usually requires an energy of 80 kcal./mole or more. The initiating role of oxygen is evident on considering the fact that pyrolysis reactions progress at a measurable rate only at 450°C. and above; oxidation of paraffins often readily occurs at 300°C.. With increasing temperature, cracking products predominate over oxidation products (38) and even small amounts of oxygen can abruptly accelerate the decomposition.

The influence of trace concentrations of oxygen on the decomposition of n-butane was first studied by Appelby et al (39). A pyrex flow reactor was operated at about 500 °C. and upto 1 atm. pressure. The decomposition was highly sensitive to oxygen; with an oxygen concentration of 0.5% the decomposition rate was increased 100-fold over the oxygen-free pyrolysis. At low oxygen concentrations the major products were hydrocarbons and water, no oxygenated hydrocarbons were found. By comparison with the normal pyrolysis the effect of oxygen was to increase the formation of ethylene and 1-butene. By extrapolating the product composition back to zero conversion they concluded that oxygen in low concentrations acted predominantly as a dehydrogenating agent, water and butenes being formed as products.

In his experiments on propane, Voevodsky (5) noted that the effect of oxygen, in a quartz reactor, was to

accelerate the reaction upto a limiting value. The effect of oxygen was dependent on the pre-treatment of the surface but was not as marked as the effect reported by Appelby et al.

Using both quartz and pyrex reactors Niclause et al (36) studied the influences of traces of oxygen on the pyrolysis of propane and of iso-pentane. In a reactor with a small surface-to-volume ratio, oxygen accelerated the reactions considerably in their initial stages, though the acceleration was short-lived. With higher surface-to-volume ratios the effect of oxygen was to inhibit decomposition such that under certain conditions the reaction was almost completely inhibited. From this severe inhibition effect they concluded that molecular decomposition mechanisms played a negligible role in the pyrolysis. A dual role of oxygen was postulated in which oxygen could catalyse the reaction by the initiation:

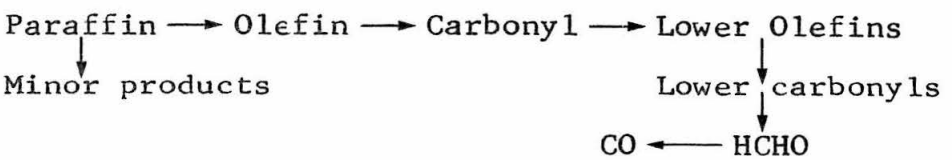
$$RH + O_2 \longrightarrow R^{\cdot} + HO_2^{\cdot} \quad \text{(a homogeneous step)}$$

Inhibition could occur when active alkyl radicals were replaced by less active chain carriers, and the new termination processes would be heterogeneous. Their data indicated that for low values of the surface-to-volume ratio the pyrolytic system would have a sensitivity towards oxygen that approached the figures given by Appelby et al.

The Partial Oxidation of n-Butane.

With an increasing proportion of oxygen in the cracking gas stream the behavior of the system cannot be correlated in terms of pyrolytic decompositions alone but allowance must be made for the presence of oxygenated free radicals. The presence of oxygen in the reacting gases enormously complicates the kinetic behavior and mechanism by providing a whole new range of labile intermediates and complex products. The partial oxidation of n-butane is concerned primarily with the decompositions involving a limited proportion of oxygen and temperatures not exceeding 550°C.. This is a very restricted part of the whole range of hydrocarbon oxidation processes. Because partial oxidation is in itself a vast field but only of indirect relevance to this thesis, only a superficial review of the most recent findings on partial oxidation will be presented.

One of the most recent advances was due to Knox (40,61) who concluded the main reaction sequence could be best described by the general scheme:



Competitive oxidation studies had shown that the conjugate olefin would be consumed at a faster rate than the parent paraffin so that the maximum concentration of olefin would

never reach a high value. Relatively high yields of carbonyls were found in the intermediate stages of alkane oxidation. In order to explain the observed reaction rates Knox had to postulate that the $HO_2^{\cdot}$ radical formed in the early stages of the reaction could be converted into a more reactive species ($OH^{\cdot}$) in the intermediate stages of the reaction. The complete description of the oxidation then required a mechanism for converting $HO_2^{\cdot}$ to $OH^{\cdot}$, an account of the stability of the intermediate peroxy and hydroperoxy radicals, and the temperature limitations which could be applied to any one conversion mechanism. The detailed scheme proposed by Knox was able to account for many aspects of partial oxidation reactions including the rapid disappearance of olefins in systems containing a high oxygen concentration, the negative temperature coefficient wherein over a short range of temperature the rate of reaction fell with increasing temperature, the importance of surface reactions, and the effects of hydrocarbon structure on the oxidation process. Thus, the scheme proposed by Knox has effectively incorporated much of the available evidence on partial oxidation (41,42,43,44) in a more comprehensive way than was possible with the earlier theories (42,43).

The Knox scheme is not without criticism however. Semenov (62) has performed computations to show that the Knox scheme does not give the acceleration from low to high rates of reaction characteristic of the progress of hydro-

carbon oxidation and that in consequence the Knox scheme predicts excessively long reaction times. Semenov further considered the formation of olefins in the early stages of the reaction to be evidence of a heterogeneous reaction which contributes proportionally less to the final product composition as the main reaction proceeds through a homogeneous, chain-branching oxidation. Albright (63) cited some observations that the product composition resulting from the oxidation of a paraffin and that from its conjugate olefin were quite different. Observations on the role of surfaces were also reviewed by Albright. Most of the construction materials used in these studies have been pyrex (64) or quartz (47) and occasionally stainless steel (47). Problems with unstable carbonaceous deposits were encountered in most studies.

Chemical shock tube experiments have permitted study of the initiation reactions which occur in extremely short reaction times (46). It appears that, at least in shock tubes, the butane decomposes pyrolytically, i.e. by mechanisms which are independent of the presence of oxygen, and that the rate of decomposition decreases sharply during the first millisecond of reaction. These workers assert that data obtained by other methods for reaction times in excess of several milliseconds cannot be extrapolated to shorter reaction times. However, workers using conventional kinetic methods have generally adopted the

initiation involving the formation of an $HO_2^{\cdot}$ radical.

Reasons for the Present Study.

The pyrolysis of n-butane has been studied intensively for some time with many conflicting results and interpretations. Although the initial product distribution is now fairly well agreed on, the kinetic parameters show considerable discrepancies. Several effects could have contributed to the disagreements in the data including spurious surface effects, heat transfer within the reactor, and the possibility of secondary reactions at high extents of decomposition. In many of the larger-scale reactor studies the thermal history of the butane was poorly defined. Workers using flow-reactors have not usually considered corrections for deviation from plug-flow. Unstirred batch reactors have very limited heat transfer characteristics, which could explain the induction periods noted by one worker (22). Studies of the effects of the surface-to-volume ratio using a batch reactor can easily be confused by the withdrawal of samples through fine capillary lines.

The effects of added inert gases on the pyrolysis system are not yet well documented. Comparisons of the effects of gases of differing atomicity could prove most interesting. In view of the results of Appelby et al (39)

that trace quantities of oxygen (ppm.) could significantly affect the reaction rate, it is most surprising that few workers have checked on the possibility of oxygen contamination in their apparatus. At higher oxygen levels (a few percent) both initiation and termination involve the presence of oxygen. At low oxygen levels it is quite possible that only the initiation will be affected, and a considerable catalysis can occur (36).

Most studies of the pyrolysis and partial oxidation of n-butane have been restricted to pressures of one atmosphere or less. Within the restricted pressure range hitherto adopted it has been possible to elucidate some of the basic physico-chemical processes. There is some incentive for constructing equipment that can be operated at higher pressures to see if the proposed mechanisms for the pyrolysis are applicable at higher pressures.

There has apparently been little interest in the way by which the carbonaceous deposits in an aged reactor can affect the decomposition process. There has been a considerable amount of work carried out in either clean or aged vessels, but very few workers have seriously attempted to correlate the decomposition behavior in the period between these two extremes (19,47). Very little is known about the chemical composition of the carbonaceous deposits and the efficacy of different film-removal agents remains

unknown. Studies on ageing could probably be best carried out using a combination of a tubular flow reactor in series with a capillary chromatographic column in a manner similar to the technique developed by Keulemans (48).

The apparatus used in the present work was designed to minimize the sources of error described above. The equipment could be used in both pyrolysis and partial oxidation studies. A continuous flow microreactor was used to investigate the thermal decomposition n-butane, both in the presence and the absence of trace amounts of oxygen. Experiments were performed over a temperature range of 529 to 595°C., a pressure range of 5 to 20 psia., and with conversions not exceeding 2%. A variety of inert gases were added to the butane stream. The arrangement provided a heating effect of the butane at the reactor inlet which was rapid in comparison with the mean contact time in the reactor. A sharp cooling effect at the reactor outlet was accomplished by addition of an inert quench gas. In this manner the thermal history of the n-butane could be well defined. The reactor tube and end sections were made of gold. Gold has not been used previously in detailed kinetic studies into the pyrolysis of n-butane and on several counts is expected to have a low surface activity (49,50). The use of small-scale equipment permitted the use of high grade materials, facility for operation at high

pressure and promoted accurate thermostatting.

The Chemical Reactivity of Gold Surfaces.

Chambers and Boudart (72) briefly reviewed the reactions in which gold surfaces are considered to play some role; none of these reactions has any immediate relevance to the pyrolysis of n-butane. They did claim however, that the gold possessed weak chemisorptive properties for some hydrocarbons and for oxygen and could act as a catalyst in oxidative dehydrogenation reactions. The adsorption of ethylene on gold has been described as a strong physical adsorption (50). In their pioneering studies using a gold reactor for cracking hydrocarbons, Keulemans et al (48) considered that there were no catalytic influences due to the surfaces.

The gold atom has a single s electron outside a completed d shell. The energy required for a d - s promotion is fairly small (3.25 ev.). Thus, a fairly easy promotion might accompany chemisorption to create d band vacancies which could be effective in chemisorption (50). An interesting paper by Mattera et al (73) indicated that the surface structure of gold (100 face) undergoes large changes with temperature in the range of typical pyrolysis work.

In a paper which is of great significance in describing the surface properties of gold, Plumb and

Thakkar (69) adduced evidence from Volta potential measurements to show that "gold surfaces may quickly become contaminated with oxides of impurity metals if a source of such impurities,either from the gold itself or from the supporting substrate, is available.". Although there is little other direct evidence to substantiate the findings of Plumb and Thakkar, thermodynamic evidence suggests that pure gold is stable in the presence of oxygen (69). Chambers and Boudart (72) concluded that the presence of impurities did not affect the catalytic activity of gold for both hydrogenation and dehydrogenation of cyclohexane.

A further serious complication in the understanding of surface effects arises because the gold is likely to be covered by both carbonaceous deposits as well as the oxides of impurities.

APPARATUS - Equipment and Design Considerations.

Introduction.

With the increasing sensitivity and reliability of analytical techniques which have been developed over the past decade it has proved possible to investigate the kinetics of complex reactions in more detail. Gas-liquid chromatography has given an enormous boost to experimental studies of reaction kinetics because it is capable of a relatively fast and direct read-out of the stable components in a gas mixture. Chromatography has, to a large extent, supplanted other established techniques such as mass spectrometric analysis and the manometric method.

These refinements in analytical techniques have permitted the development of the microreactor. The term "microreactor" has been coined to cover several types of equipment which are characterised by their small size and, often, by the small conversion which is effected. In the context of the present discussion the term "microreactor" will refer to a tubular, continuous-flow reactor operated under steady-state conditions. Two related techniques are the microcatalytic reactor developed by Emmett et al (55) and the system used by Keulemans et al (48) in which the reactor and chromatographic column are directly connected. The system used by Keulemans is very useful for establishing the cracking patterns of various hydrocarbons but suffers

from inflexibility and innacuracy for detailed kinetic studies when compared with the continuous-flow reactor.

The microreactor used in the present study had an internal diameter of 0.0625 in. and a length of 12.0 in.. Comparable figures for the more conventional reactor used by Wang et al were 1.0 in. and 30.0 in. respectively. The advantages of using the microreactor may be summarised as:

a. The reactor is easily thermostatted.

b. The small scale permits economic use of high-grade materials, both for the reaction under study and for materials of construction. This is a significant criterion when high-temperature degradation of conventional construction materials can occur.

c. The high length-to-diameter ratio serves to minimise end effects and favors the use of the plug-flow assumption.

d. Interchanging of reactor components is facilitated. A single unit can accomodate a reactor length of a few inches or of several feet.

The disadvantages of using the microreactor are:

a. One cannot conveniently insert probes for heat- or mass-transport studies in the reactor. The plug-flow assumption can be justified but not demonstrated.

b. A small bore reactor has a high surface-to-volume ratio which packing can only increase. If there is reasonable doubt as to the conditions under which the

decomposition may be considered homogeneous, then the microreactor is unsuitable for demonstrating the homogeneity of the reaction, particularly at low pressures.

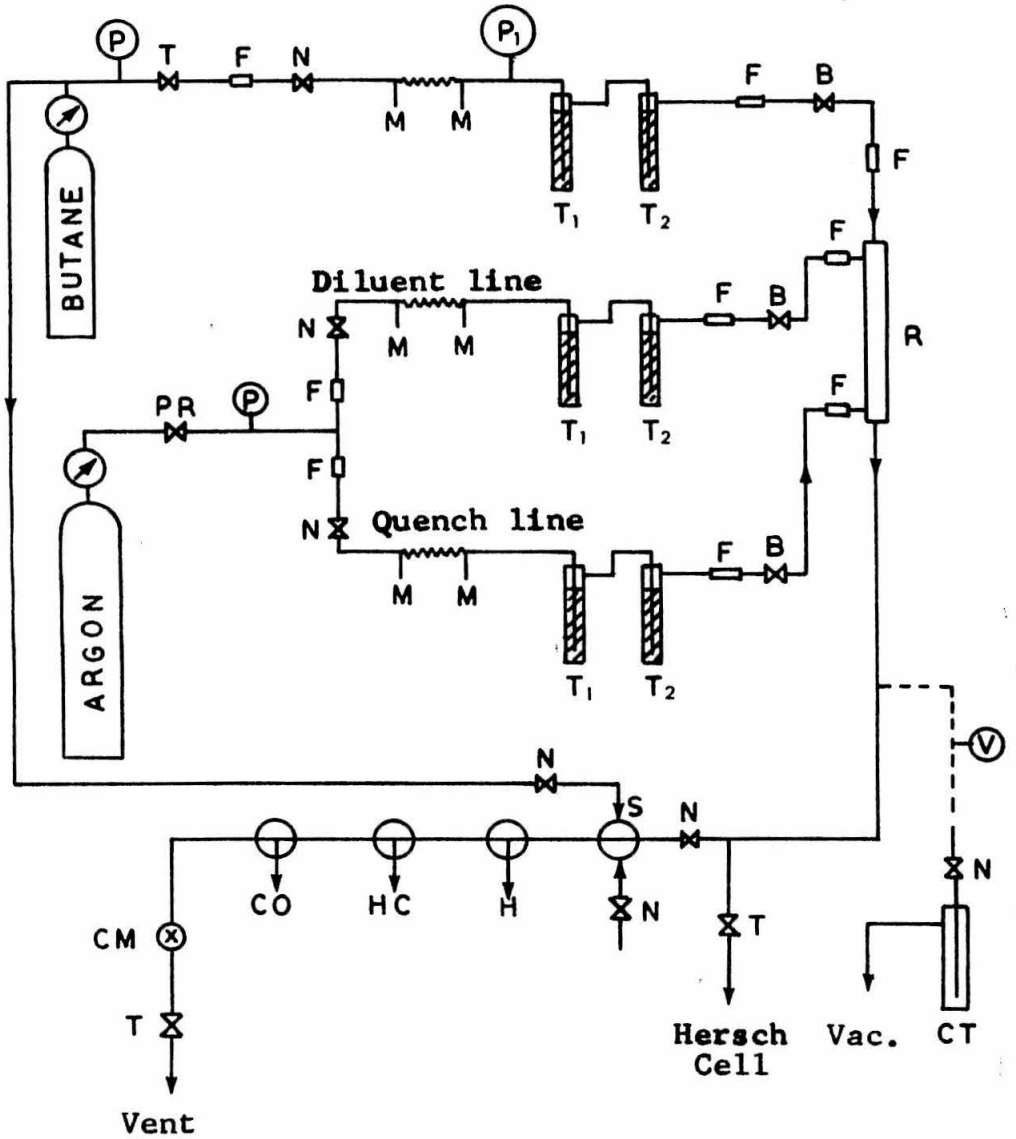
c. Tubular flow-reactors have a common disadvantage in that there is a distribution of residence times. In "feed-back systems", typified by the pyrolysis of butane, the decomposition can be influenced by the products of reaction such as propylene and carbonaceous deposits. The quantitative correction for the effects of those products on a system with a large distribution of residence times may be difficult, or impossible, to estimate.

d. One cannot satisfactorily inspect, visually or by many other means, the surface of a small bore-reactor.

Flow-Control for the Microreactor.

The accompanying schematic indicates the layout of the reactor and auxiliary components. Several considerations which were peculiar to the operation of the microreactor affected the selection of flow-contollers and flow-meters.

The flow-rates of the various gas streams were set by small-bore needle valves (Nupro, Type 1SA). Typically with a pressure drop of about 2 psi. across the valve the flow-rate of gas could be satisfactorily regulated in the range 0.5 to 10.0 ml./min.. The upstream pressure regulation was



Legend:

P	Pressure gauge	R	Reactor
P_1	Reactor pressure gauge	V	Vacuum gauge
T_1	Toggle valve	S	Selector valve
F	Filter	H	Hydrogen analysis valve
N	Needle valve	HC	Hydrocarbon analysis
PR	Pressure reducer	CO	Carbon dioxide analysis
T_1	Water trap	CM	Cartesian manostat
T_2	Oxygen trap	CT	Cold trap
M	Manometer connections from packed columns	B	Bellows valve

Figure 1. Schematic of reactor and component layout.

performed with conventional cylinder regulators (Matheson). For convenience, a panel-mounted regulator was also incorporated into the inert gas stream (Kendall, Model 30).

A cartesian manostat (Manostat Corporation, No. 6A) was used to regulate the reactor pressure. This device was capable of controlling the pressure at the low flow-rates of gas to within 0.05 psia of its set point over the range of pressures which were studied (5 to 20 psia.). Mercury was used as the manostat fluid. One problem was encountered in using the manostat. When a gas stream which was super-saturated with water was regulated by the manostat, the water would collect in the manostat and interfere with the free operation of the float. A trap of Anhydrite was installed upstream of the manostat. Ordinarily the reactor effluent would be vented to the atmosphere. For operation at sub-atmospheric pressures a vacuum-pump would be coupled to the manostat. Venting to either the atmosphere or to a vacuum did not significantly affect the set-point of the manostat.

The pressure in the reactor was measured using a calibrated Bourdon-tube gauge (Wallace and Tiernan, Type FA-145). The location of the point at which the pressure of the reactor was taken reflected a compromise between accurately measuring the pressure and the need to trap out any impurities which may enter through the gauge and its connections.

Metering of the flow of gas to the reactor was adequately accomplished by measuring the pressure drops developed over packed columns. For the inert gas streams the packed columns were 0.18 in. internal diameter and 15 in. long; the column for the butane stream was 0.086 in. diameter and 15 in. long. Glass beads (Minnesota Mining and Manufacturing Co., Type 100-5005) were used as the packing material. Because the flow resistance of a packed column has a significant temperature coefficient the columns were thermostatted together and maintained at a temperature of 27°C. $\pm$ 0.05°C.. Conventional manometers were used to measure the pressure drops across the packed columns. Silicone oil (Dow-Corning, Type 200-500) was selected as the manometric fluid because of its suitable flow characteristics and its low vapor pressure. The silicone oil was degassed by heating to 70°C. under vacuum before adding it to the manometers; it is well known that selective absorption and desorption of gases can lead to errors in the manometer readings. Catch-pots were installed on the manometer connection lines to prevent any blow-over of fluid into the reactor feed lines in the case of an inadvertent surge of gas through the system. Although for reliable start-up tests on a reactor the dead-volume in the flow-metering system should be minimised, attempts to reduce the dead-volume by using narrow-bore manometers were not satisfactory. A further problem, peculiar to the

butane flowmeter, was that if the total pressure of the system was reduced rapidly to about 4 psia. the silicone fluid would de-gas rapidly and the violent foaming action which was induced would expel the fluid over into the catch-pots. To break up the foam the manometer was made with a bulb at the top of each leg. Each flowmeter was calibrated against a soap-bubble flowmeter to which a correction for the presence of water vapor was applied. Calibrations were usually quite linear and did not depend on the total pressure of gas over the pressure range studied. The calibrations were reproducible to within 2% over a period of several months. Compressibility factors were applied to the flow of butane at pressures above atmospheric. The inert gases were treated as being ideal gases.

To facilitate de-gassing operations on the reactor, bellows valves were installed on the feed lines to the reactor. These valves (Nupro, Type SS4BG) were leak-tight and capable of a hard shut-off. When de-gassing of the reactor was to be carried out, the reactor outlet was uncoupled from the sampling train and connected to a vacuum pump. The pump was capable of reducing the pressure in the reactor down to about 1 micron. A hot-wire gauge (Televac) gave an indication of the de-gassing pressure.

Liberal use was made of filters (Nupro, 7 micron elements) to protect all critical valves and to keep

particulate matter out of the feed lines to the reactor.

Purification of Feed Gases.

Oxygen and water were removed from all feed gases. Oxygen because of its marked influence on the pyrolysis and water because of its uncertain contribution to the oxygen mass-balance in partial oxidation studies. No other reactive inorganic species were ordinarily present in the feed gases. The feed gases were n-butane (Phillips, Research grade) and an inert gas (argon, nitrogen, helium or carbon dioxide) which was usually of 99.99% minimum purity (Linde).

Water was removed from the inert gas stream by traps of indicating silica-gel. Anhydrite was used to dry the n-butane stream because it was found that silica-gel had some unpredictable adsorption tendencies which affected the flowrate of butane through the traps. Oxygen was removed using traps of manganous oxide. The operation and regeneration of the oxygen traps is discussed in an appendix to this thesis (Appendix 5).

The isomeric butenes are minor products in the pyrolysis of n-butane and have an uncertain influence on the kinetics of both pyrolysis and partial oxidation processes. Consequently, in some experiments, butene-free feed was used. Research grade n-butane ordinarily contained several hundred ppm. of each butene isomer and iso-butane as impurities. A system was assembled to scrub out traces

of butenes from the butane by the action of concentrated sulphuric acid. The treatment converts the butenes to soluble butyl alcohols and higher products. The n-butane was contacted in a single-pass scrubber which contained 90% sulphuric acid. Virtually complete removal of the cis- and trans-2-butenes and of 1,3 butadiene was achieved but removal of 1-butene was typically only 80% complete. The efficiency of the absorption was not affected on raising the temperature of the scrubber from 25 to 45°C.. The acid-scrubbed butane was passed through dilute alkali and then through distilled water. The gas was then dried using a column of Anhydrite and was finally collected in a recieving cylinder held at Dry Ice temperature.

The Sampling Train.

Separate sampling arrangements were necessary for the analysis of oxygen by the Hersch cell and for the gas-chromatographic determinations of hydrogen, hydrocarbons and carbon dioxide. Because of its extreme sensitivity to oxygen, the Hersch cell was mounted upstream of the chromatographic sampling points to avoid errors caused by the cross-contamination of the reactor effluent by the various carrier gas streams. The sampling valve for the hydrogen analysis was mounted upstream of the valve for hydrocarbon determinations because any leakage of the helium carrier used for hydrocarbon determinations would

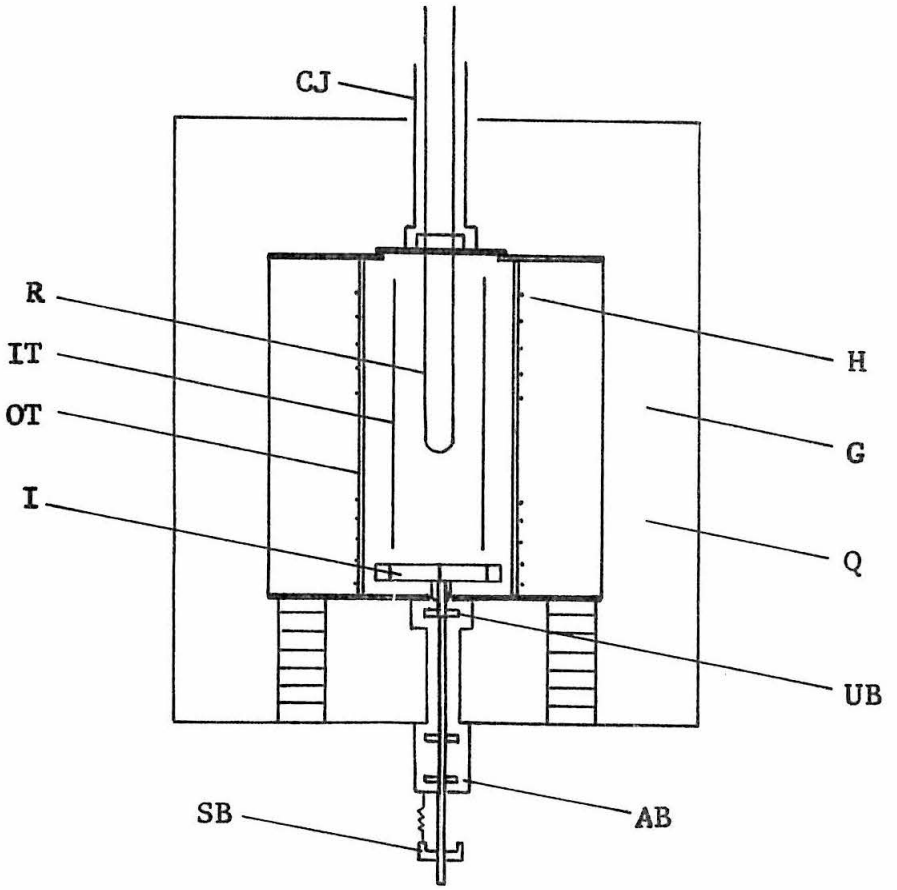
have been erroneously read-out as hydrogen. A selector valve (Circle-Seal, Model P4-418T) was used to permit samples of the n-butane or of a calibration gas to be run through the analytical train. Operation of the Hersch cell and of the several chromatographs is described in appendices to this Thesis (Appendices 4 and 5).

Design of the Thermostat.

The basic requirements of a thermostat were that it should be capable of operation upto 600°C. with minimal temperature gradients, it should be large enough to accomodate a long tubular reactor (coiled if necessary), and it should provide for easy accessibility of reactor tubes and other components. Attention was focussed on oven designs in which the temperature gradients are minimised either by judicious placement of the heaters or by a rapid recirculation of air through the thermostat. Stainless steel was used in the construction of the majority of the high-temperature components. A cooling jacket was installed to keep the inlet and outlet lines cool relative to the reactor temperature so that reaction in those lines was minimised. This precaution should have permitted a more precise estimate of the effective length of the reactor, in practice the cooling jacket was primarily responsible for the temperature gradients within the thermostat.

Much time was spent in the early stages of this study in the development of a recirculating-air thermostat of the type shown in the accompanying figure. By rotating the impeller at about 1500 rpm. a rapid recirculation of air resulted in virtually complete elimination of the temperature gradients in the thermostat. The alignement and loading bearings were mounted in order to reduce the rate of wear of the upper bearing. Despite these precautions, and despite the use of a high temperature lubricant (Tungsten disulphide, Bemol Corp.) the upper bearing wore out every few weeks and proved to be the major factor in reactor down-time. Evidently, one of the major factors in the rate of wear of the bearing was the accumulation of surface scale and particulate matter in the housing of the bearing. The bearings used were stainless steel (New Departure, No. SS/R4A); carbide bearings may have permitted longer periods of operation. The impeller had 10 straight blades and was machined from a single block of stainless steel and press-fitted to the drive shaft. It proved to be both convenient and economic to replace the recirculating air thermostat by a unit which relied on conductive transmission of heat to reduce the temperature gradients.

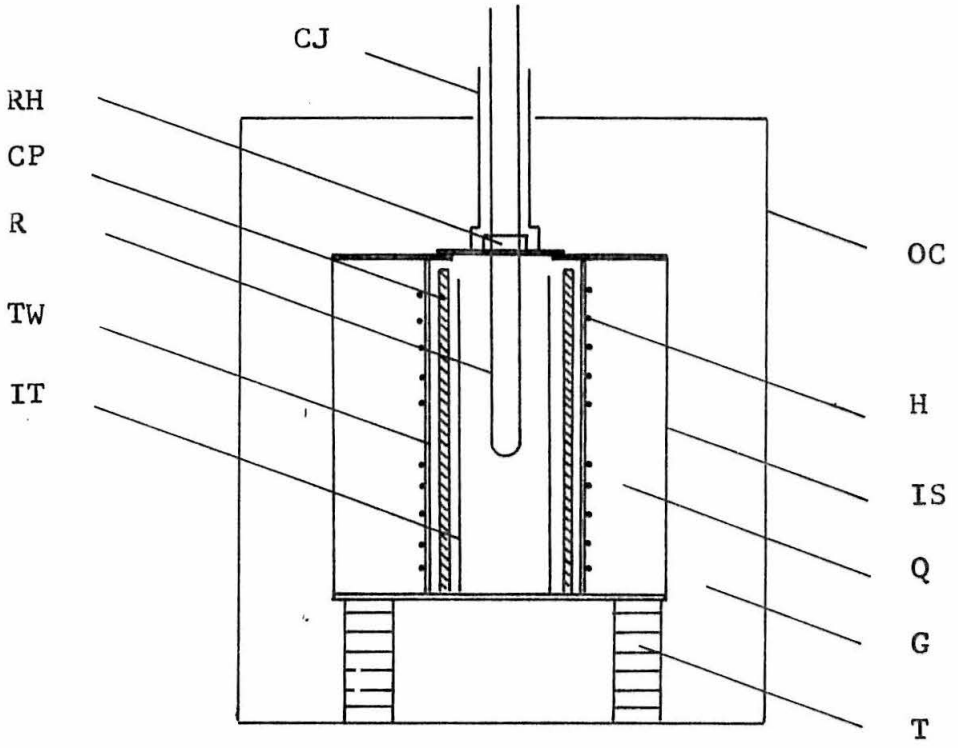
The final assembly of the thermostat is shown in Figure 3. The thermostat walls and the bottom and support plates were made of stainless steel (Type 321 and 304)



Legend:

CJ	Cooling jacket	H	Heating element
R	Reactor	G	Glass fiber
IT	Internal tube	UB	Upper bearing
OT	Outside tube	AB	Alignement bearing
Q	Quartz fiber	SB	Support bearing
I	Impeller		

Figure 2. Layout of Recirculating-Air Thermostat.



Legend:

CJ	Cooling jacket	OC	Outer case
RH	Reactor head	H	Heater
R	Reactor	Q	Quartz fiber
TW	Thermostat wall	IS	Insulator supports
IT	Internal tube	T	Transite blocks

Figure 3. Layout of Conductive Thermostat.

and the assembly was heli-arced together. Stainless steel rods were employed to provide a conductive transport of heat through the thermostat. For work below 550°C., rods of aluminum-bronze could be used in place of the stainless steel rods, the former having a much higher conductivity.

Two beaded heaters (Cole-Parmer, 400 watt each) were wrapped onto the circumference of the thermostat wall. These heaters were long (12 ft.) and the low watt/inch rating made it possible to bring the elements directly out to low temperature terminals with a minimum of heat wastage. Sheathed heating elements had been used and found less satisfactory mainly due to the problem of making suitable high temperature terminals. A small cartridge heater (50 watt) was also mounted in the cooling jacket. The voltage to this heater would be adjusted so that the temperature of the reactor head-block was about 15°C. cooler than the thermostat temperature. Any larger difference in the two temperatures would have caused severe gradients in the thermostat.

Chromel-alumel thermocouples were inserted at various points in the thermostat. These thermocouples (Ceramo, 0.125 in. diameter, sheathed) were calibrated at the tin, lead and zinc points using A.C.S. grade materials. The calibrations compared satisfactorily with N.B.S. standards. The thermocouples were biased against an ice-point

reference and were read-out to ± 0.005 mv. using a potentiometer (Leeds and Northrup, Type K-3).

Quartz fiber was used as the high temperature insulator. A further layer of glass fiber (3 in. thick) was placed around the quartz fiber so that at no point was the total thickness of insulation less than 4½ in.. The whole thermostat assembly was placed inside an aluminum box and mounted in a "Unistrut" frame from which it could be easily removed for maintenance.

Power for the thermostat was drawn from a regulated source and was set by Variacs. With typical fluctuations in room temperature and voltage supply the variation in the thermostat temperature was ± 2°C. and rarely drifted by more than 1°C. in a one hour period. To take the thermostat upto 570°C. a total power input of about 0.5 kw. was required. The thermostat was never operated above 595°C. because silver-soldered joints were used in the construction of the reactor head.

Reactor Tube and Head Assembly.

The important concepts in the design of a suitable head assembly for the reactor were:

1. To ensure that the hot butane contacted only gold surfaces.
2. To provide sharp heating and cooling effects of the butane by the diluent and quench gases.

3. To make a unit in which reactor tubes of differing length and diameter could be mounted.
4. To ensure absolute leak tightness.
5. To ensure the purity of the gold.
6. To minimise heat losses from the reactor thermostat.

The accompanying figure shows the construction of an inlet head which was used in the preliminary studies on the pyrolysis of n-butane. It was extremely difficult to ensure that the fittings did not sieze and yet maintain satisfactory leak-tightness. A gold-seal arrangement with tungsten disulphide lubricant on the fittings proved to be satisfactory. Compression fittings (Swagelock) could be used on the gold reactor tube if the front ferrule was silver-soldered to the tube; these fittings were prone to seizure. The preheat line for the diluent was a stainless steel tube. The design of the outlet head was very similar to that of the inlet head. This system was abandoned in favor of an all-gold reactor when suspicions grew that surface scale from the hot diluent line was being carried over into the reactor and contaminating the gold surfaces. Another problem with the stainless steel diluent line was that in the studies using trace levels of oxygen, some of the oxygen would be removed by the hot stainless steel tube so that the level of oxygen which entered the reactor could not be satisfactorily determined. Furthermore, in order to carry out the acid-etch treatment of the gold, which later work

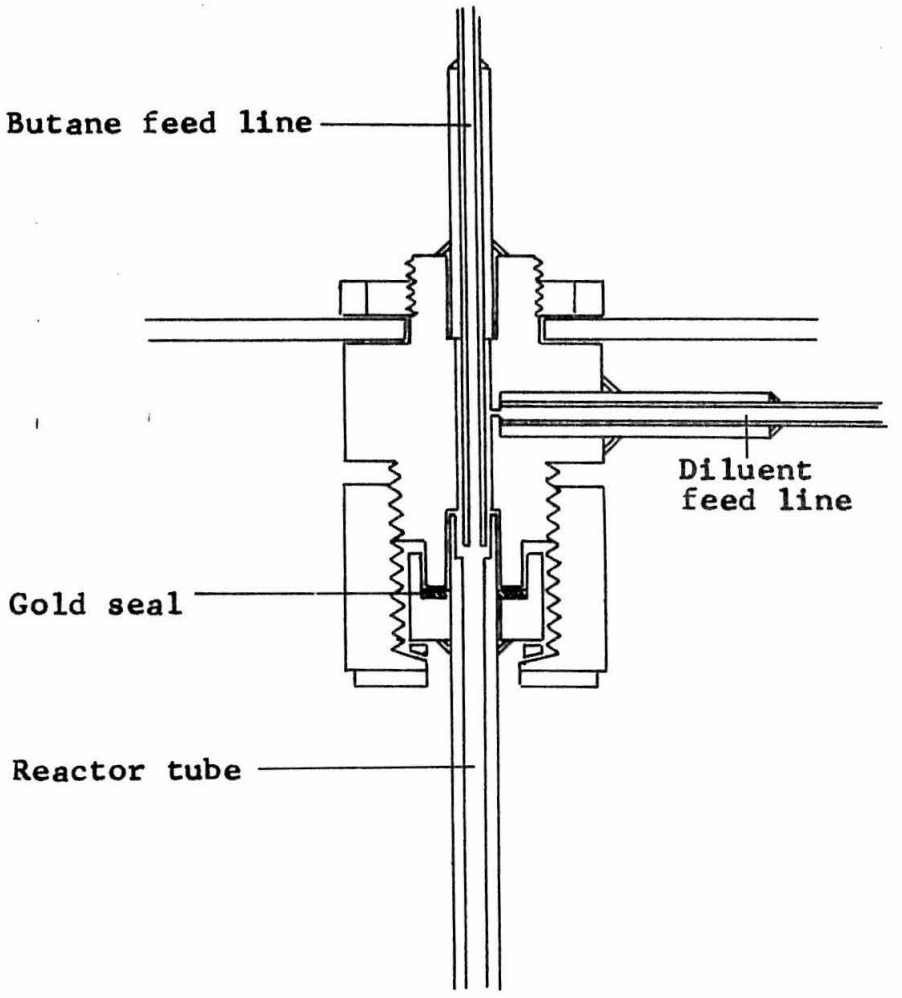
necessitated, the reactor system would have to be taken apart for each treatment.

An all-gold system was built to remedy the deficiencies of its predecessor. After passing through filters (Nupro) in the feed lines the gases contacted only gold. This system also permitted the acid-wash operation to be carried out on the reactor in situ. The inlet and outlet lines were gold capillary tubing (0.03 in. i.d.) and were supported by stainless steel sheaths. The remainder of the construction is evident from the accompanying schematic. All crucial joints in the assembly were heli-arced, the only silver-soldered joints were for mounting the protective stainless steel tubes and were not crucial to the leak-tightness of the assembly. Great care was necessary in fabricating the heli-arced joints because any inadvertent contact of the arc onto the end of a capillary tube would immediately close the end of the tube. The gold used in the construction of the reactor was 99.99% pure gold (Wilkinson). The assembly was supported in a large stainless steel block. The block proved to be a major factor in inducing temperature gradients in the ends of the reactor.

An improvement over the present construction would be to use heavy-wall gold castings for the inlet and outlet sections of the reactor. The increased wall thickness of a casting would give extra support to the heli-arced joints and would reduce the chances of accidental crushing

and cracking of the tubing. Suitable castings could be prepared by fusing gold chips into a graphite block though care was needed to eliminate all air pockets from the casting. The support block needs re-designing because of its large but unpredictable contribution to the thermal gradients in the ends of the reactor.

Gold microspheres could be prepared to be used as packing for the reactor. On heating short sections of gold wire to the melting point, the surface tension of the liquid would draw the gold into a sphere. A section of ceramic tubing was used to support the pieces of gold wire which were then heated indirectly by an oxy-acetylene flame. Microspheres (0.02 in. dia.) prepared in the fashion had satisfactory surface smoothness.



(Scale: 2 x actual size)

Figure 4. The Inlet Head of the Reactor - First Assembly.

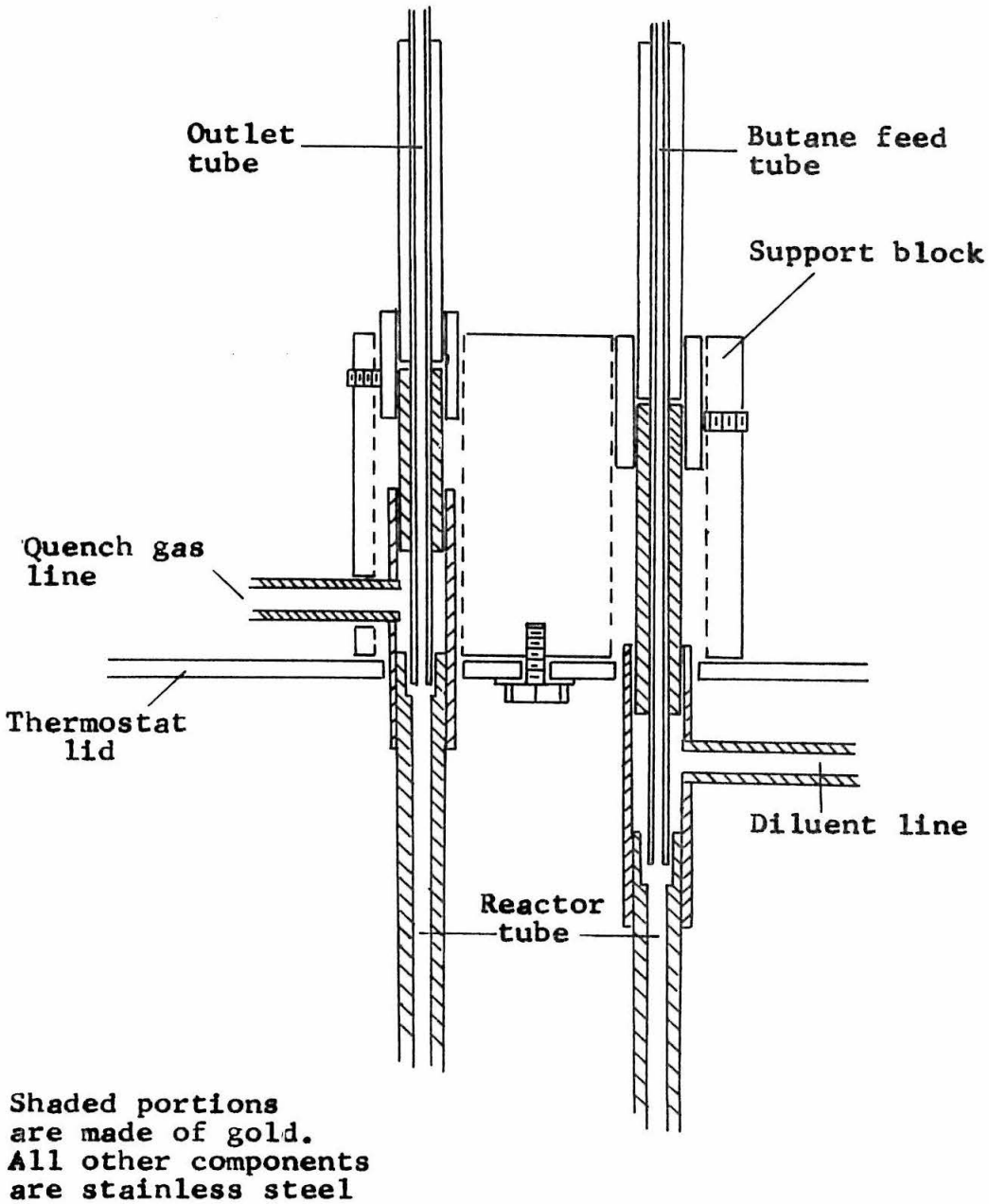
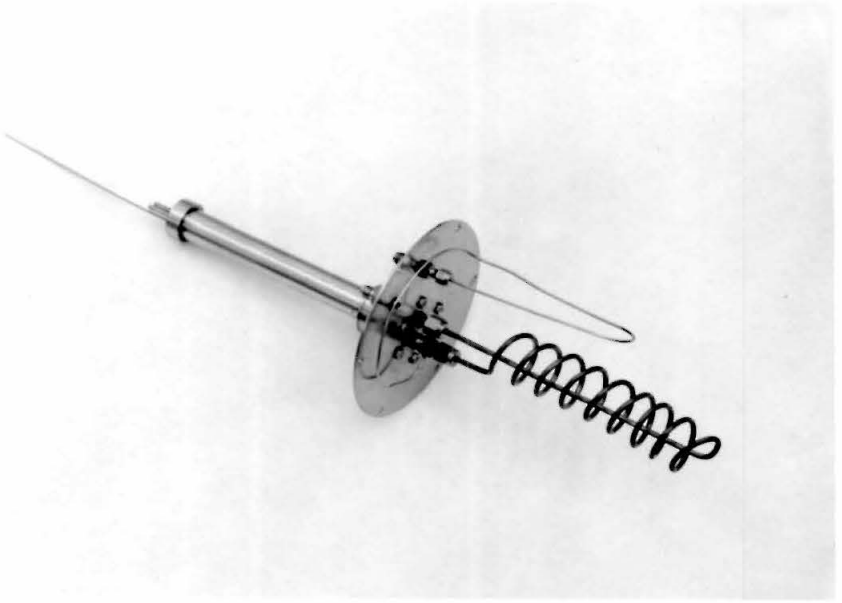
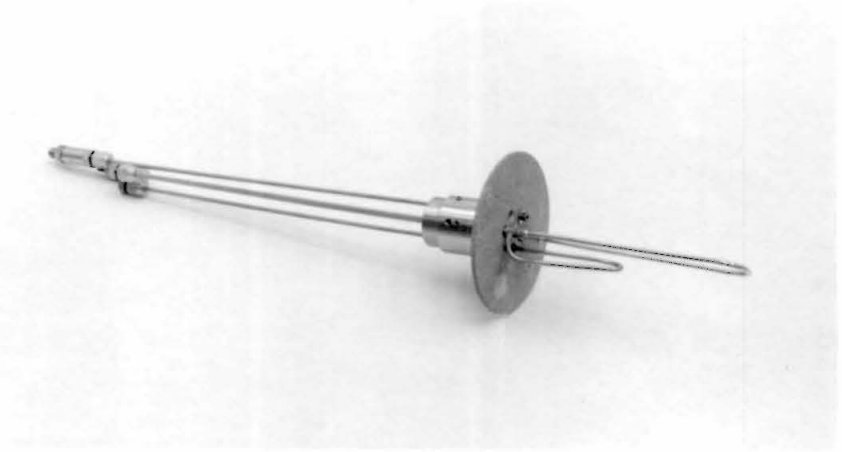


Figure 5. The Reactor Head - All-Gold System



The original reactor assembly.



The all-gold reactor assembly.
(Cooling jacket is not shown).

SUMMARY OF THE EXPERIMENTAL PROGRAM.

In the course of this study the following variables were investigated in both pyrolysis and partial oxidation reactions: temperature, total pressure, partial pressure of n-butane, mean contact time, type of diluent gas, and in some start-up studies the reactor pretreatment and time of operation were noted.

The study was divided into several series of runs, each series having its own limited set of objectives. In chronological sequence, the major objectives and conclusions of the series were as follows:

Series 1 to 5.

Preliminary series where a suitable range of conditions was outlined for a study of the pyrolysis. Major equipment problems (due to leakage and temperature gradients) were encountered in this early work. Results showed that the observed conversion did not depend on the flow-rate of the quench gas.

Series 6.

A systematic study of the pyrolysis of n-butane was undertaken. Argon was the diluent gas. The reactor was an untreated gold tube. The variation of the rate with temperature and partial pressure of butane was studied. The product composition was shown to compare satisfactorily

with the results of previous workers.

Series 7.

Study of the pyrolysis using a packed reactor and comparison of the results with Series 6.

Series 8.

Partial oxidation of n-butane.

Work at trace levels of oxygen was followed by a set of runs in which the variation in product yield with temperature, pressure, oxygen level and contact time was studied. The role of butenes as the main intermediaries in the partial oxidation was demonstrated. Irreversible effects of oxygen treatment of the reactor surfaces were found to affect the pyrolysis.

Series 9.

Chemical treatments of the gold surfaces and their effects on the pyrolysis were studied. The possibility of surface contaminants in the gold, especially the oxides of impurity metals, was proposed to account for the variation in the pyrolysis behavior.

Series 10.

The all-gold reactor system was used in this and all subsequent series. The effects of chemical treatment of gold surfaces were again checked. An acid-treated reactor gave reproducible pyrolysis behavior.

Series 11.

The effects of temperature gradients in the thermo-

stat were shown to be significant. Pyrolysis was carried out with a nitrogen diluent.

Series 12.

Pyrolysis at high dilution of the butane was carried out with several diluent gases. The behavior of the pyrolysis was independent of the type of diluent gas.

Series 13.

The effects of various contaminants on the pyrolysis. The inhibitory role of propylene and the inert behavior of hydrogen, ethane and the butenes were demonstrated. A further set of partial oxidation runs was performed to check on the results of Series 8.

TREATMENT OF THE DATA.

The raw data needed to define the pyrolysis system were: the dimensions of the reactor, the flowrates of the butane, diluent and quench gases, the temperature, the total pressure, and in some start-up experiments the time after start-up and type of reactor pretreatment. The composition of the effluent gas was defined by the peak areas of the chromatographic read-out.

From the total pressure and the flowrates of butane and diluent the partial pressure of the butane in the reactor was calculated directly. The mean contact time was defined as:

$$\bar{\tau} = \frac{\text{reactor volume}}{\text{total flowrate of gases (at T)}}$$

and assumed a plug-flow model and ignored expansion of the gases due to reaction.

The treatment of chromatographic data for hydrocarbons was as follows. From the individual peak areas the peak area of each component relative to that of n-butane was evaluated. The relative proportion of each component in the effluent could then be evaluated:

$$\text{Relative moles of component} = \frac{\text{moles of component}}{\text{moles of butane}}$$

$$= \frac{\text{peak area of component}}{\text{peak area of butane}} \times \frac{1}{R_i}$$

R_i is the relative molar response for component i on the flame-ionisation detector.

The relative moles of the components determined in this work are recorded in Appendix 1. The sum of the relative moles of components (Σ) was evaluated. It was not feasible to pre-set the reactor conditions exactly to the desired values and so, in order to reduce the graphical representations to a convenient number of parameters, the value of Σ was corrected for temperature, pressure and contact time. The temperature correction for pyrolysis assumed an activation energy of 65 kcal./mole and was about 4% per degree of error. The pressure correction assumed a 3/2-order dependence on the partial pressure of butane and zero dependence on the partial pressure of the diluent. The correction for errors in the contact time assumed the conversion to be proportional to the contact time. If in any run the total correction to be applied to the value of Σ exceeded 15% that run would not be included in the graphical representations.

The overall rate of reaction was defined as the total rate of product formation and is given by the expression:

$$\text{rate of reaction} = \frac{1}{\bar{\tau}} \times \Sigma_C \times p \quad \text{(psi./sec.)}$$

The rate of decomposition of the n-butane is satisfactorily taken as being half of the rate of total product formation. This assumption is valid if the major products of the pyrol-

ysis are formed by the overall reactions:

$$C_4H_{10} \longrightarrow CH_4 + C_3H_6$$

$$C_4H_{10} \longrightarrow C_2H_4 + C_2H_6$$

and also if the formation of minor products is negligible. For a more complete account of the rate of decomposition of the butane it would be necessary to perform a mass-balance calculation. In this study, mass-balance computations could not be made accurately because a small error in the flowmetering of the quench gas stream would have an effect on the overall accuracy of the balance. It was much simpler, and more reliable, to calculate out the conversion using the butane peak as a basis for calculating the relative molar conversions of the various components, and then to utilise the fact that at low conversions the peak area of the butane was proportional to the partial pressure of butane in the reactor.

In the graphical representations of the data the term "rate of reaction" refers to the initial rate of formation of products at short contact times. The term "partial pressure" refers to the initial partial pressure of butane in the reactor as calculated from the flowrates of the gases entering the reactor. With typically less than 1% decomposition of the decomposition of the butane the errors involved in equating the overall rate with the initial rate were negligible.

DISCUSSION OF THE EXPERIMENTAL RESULTS.

Introduction.

This section will present a step-by-step discussion of the experimental results which are tabulated in Appendix 1. The results will be discussed in an approximately chronological sequence so that the steps involved in the gradual refinement of the equipment are made evident. Appendix 1 contains only the reproducible data; data from the preliminary series are not included. In the preliminary series (1 through 5) the irreproducibility was partly caused by ill-defined temperature gradients in the thermostat. There were serious leaks in the first reactor assemblies which gave uncertain levels of contamination by oxygen. The presence of significant amounts of butenes in the products in the preliminary series was clear indication of contamination by oxygen. With reliable exclusion of the oxygen the yields of butenes were very low (about 1% of the products). The only other significant findings from the early series were that the conversion did not depend on the flowrate of the quench gas, i.e. there were no important mixing effects in the outlet end of the reactor. A further finding was that the conversion was approximately proportional to the mean contact time.

The reactor system used in Series 6 through 9 was the assembly which used a stainless steel diluent line. The all-

gold reactor was used in Series 10 through 13.

SERIES 6.

This was the first series in which a systematic study of the pyrolysis of n-butane was accomplished using a gold reactor. A new reactor tube was used for this series. Apart from a wash with acetone the gold tube was not subjected to any treatment prior to mounting in the thermostat. The first runs were start-up runs in which, with all other variables steady, the butane stream was turned on and the ensuing pyrolysis was checked at intervals of 15 minutes. Although the data were somewhat erratic the start-up runs (runs 1 to 6) showed that the reactor reached a steady-state condition well within 1 hour after start-up. In any start-up experiment the time required to reach a steady-state depends on the unswept volume in the system as well as any changes that are occurring in the reactor behavior. About 15 minutes were required to attain a steady flowrate of butane and to sweep out the lines and traps in the apparatus. Consequently, the variation in the rate of pyrolysis in the first two runs (taken at 15 and 30 minutes) could not be unambiguously attributed solely to effects in the reactor. Long-term drifts in the rate of pyrolysis can be safely attributed to changes in the reactor system which may be influenced by, for instance, carbonaceous deposits. The main conclusion which could be drawn from

these first start-up tests was that if there was any significant start-up effect then the effect could not be followed satisfactorily using the apparatus as it stood. Probably the formation of carbonaceous deposits was a slow process with the low conversions used in the butane pyrolysis. In that case, the above would be indirect evidence to show that the start-up effects in the reactor were negligible.

Following the start-up test a systematic series of runs was undertaken to check the rate of pyrolysis of n-butane at various partial pressures and temperatures. The accompanying plot (Figure 6) is a summary of data taken over several days operation. Several of the data points refer to check runs which were taken on separate days to check on long-term drift. The data clearly indicate that no such drift could be detected over a period of several days. Figure 6 shows:

a. The rate of formation of products was proportional to the partial pressure of n-butane raised to the 3/2 power.

b. At low partial pressures of butane, with an excess of the argon diluent, the rate of reaction apparently became first-order with respect to the butane. The change in order at lower pressures of the butane will be referred to in all subsequent discussion as the "break-off effect".

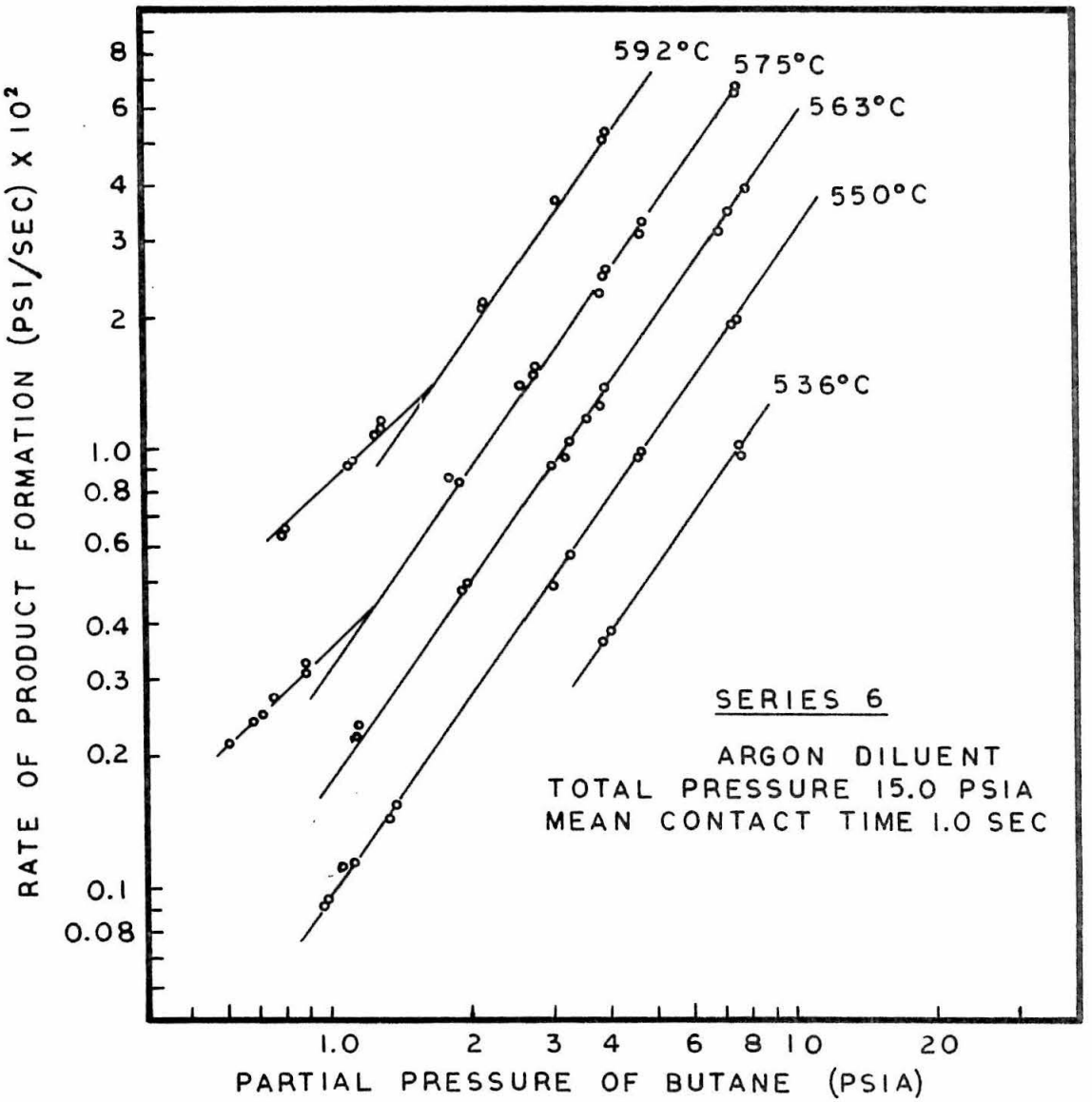


Figure 6. Rate of pyrolysis of n-butane as a function of temperature and pressure.

c. The reproducibility of the data was better than 3%.

Figure 7 is an Arrhenius plot. The rate of pyrolysis at a pressure of butane of 3 psia. was plotted as a function of the reciprocal temperature. From this figure, which showed good linearity, the activation energy of the pyrolysis was 64.1 kcal./mole. This value was significantly higher than the estimates of Sagert and Laidler and of Purnell and Quinn who reported about 60.0 kcal./mole.

Runs 32 to 35a were the first attempts to accurately demonstrate the effect of varying contact time on the conversion. Figure 8 summarises those runs. With increasing contact time there was evidently a significant fall-off in the rate of pyrolysis; the fall-off was of a magnitude that was not accounted for by the consumption of n-butane. Propylene, a major product of the decomposition, is well known to exert an inhibiting effect on the decomposition. It is tempting therefore to ascribe the fall-off in the rate to the inhibitory role of propylene. An additional factor could be that if there were any significant heat- and mass-transfer effects in the reactor, those effects would be related to the flowrate and hence to the contact time. Specific data for the inhibitory role of propylene were not taken until Series 13. Figure 8 indicates that with more than 2% of butane decomposed the inhibitory effect on the total conversion was pronounced (about 10%).

The remaining figures drawn for Series 6 refer to the

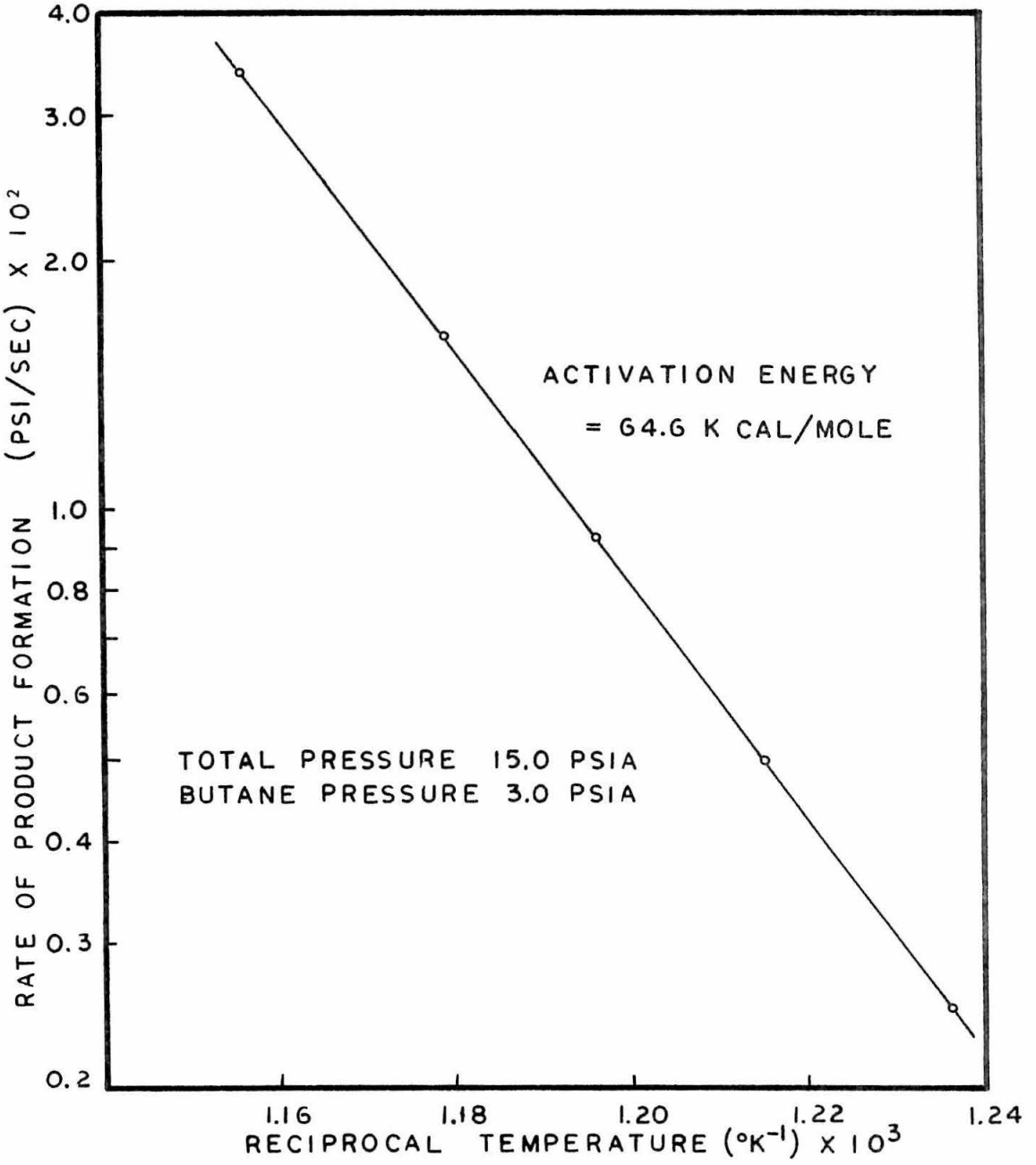


Figure 7. Arrhenius plot for Series 6.

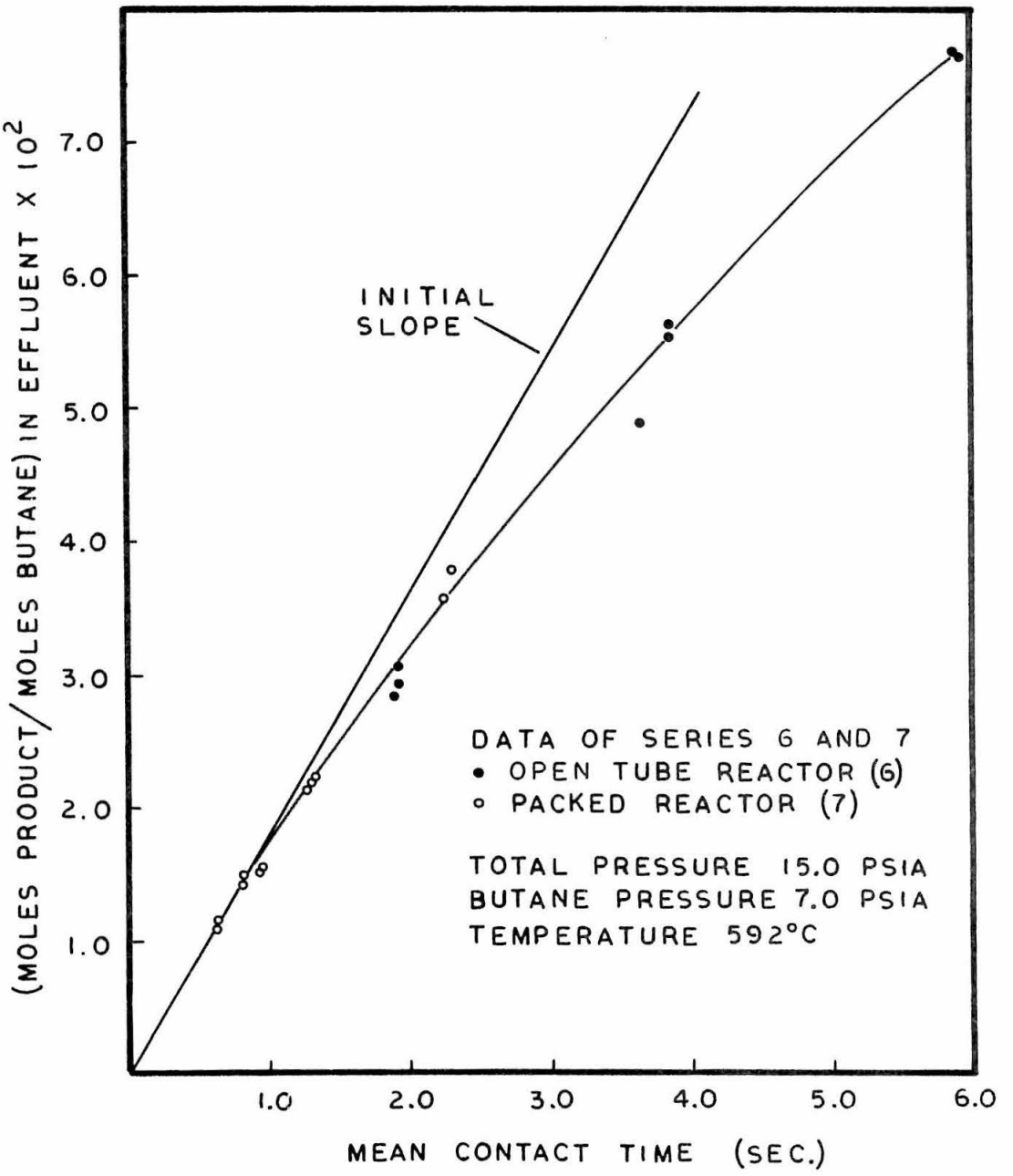


Figure 8. Plot of the total yield of products against the contact time.

variation in the product composition with changes in temperature and pressure. Purnell and Quinn (19) defined α as the ratio of ethylene to ethane in the products of pyrolysis. The variation of α with temperature and pressure was significant in describing the behavior of the ethyl radical under typical pyrolysis conditions. Figure 9 plots the variation of α with temperature and pressure. The group $(\alpha - 1)p$ was a function of p as indicated in Figure 10. An Arrhenius plot for the group $(\alpha - 1)$ at various partial pressures of n-butane is given in Figure 11. The variation of α with temperature and pressure was in good qualitative agreement with the data reported by Purnell and Quinn (19). They gave an activation energy for the $(\alpha-1)$ group as 20.7 kcal./mole at 150.8 mm.pressure; this study gave 19.7 kcal./mole at both 51.8 and 207 mm..

The total proportion of C_2 hydrocarbons in the product was a weak function of the temperature. Following Purnell's definition:

$$\beta = \frac{2\,(C_2H_4 + C_2H_6)}{(CH_4 + C_3H_6)}$$

Attempts to determine an activation energy for β were somewhat inconclusive because of the considerable scatter in the data. An activation energy of 1.5 ± 0.5 kcal./mole could be tentatively assigned to the temperature dependence of β, in satisfactory agreement with Purnell's estimate

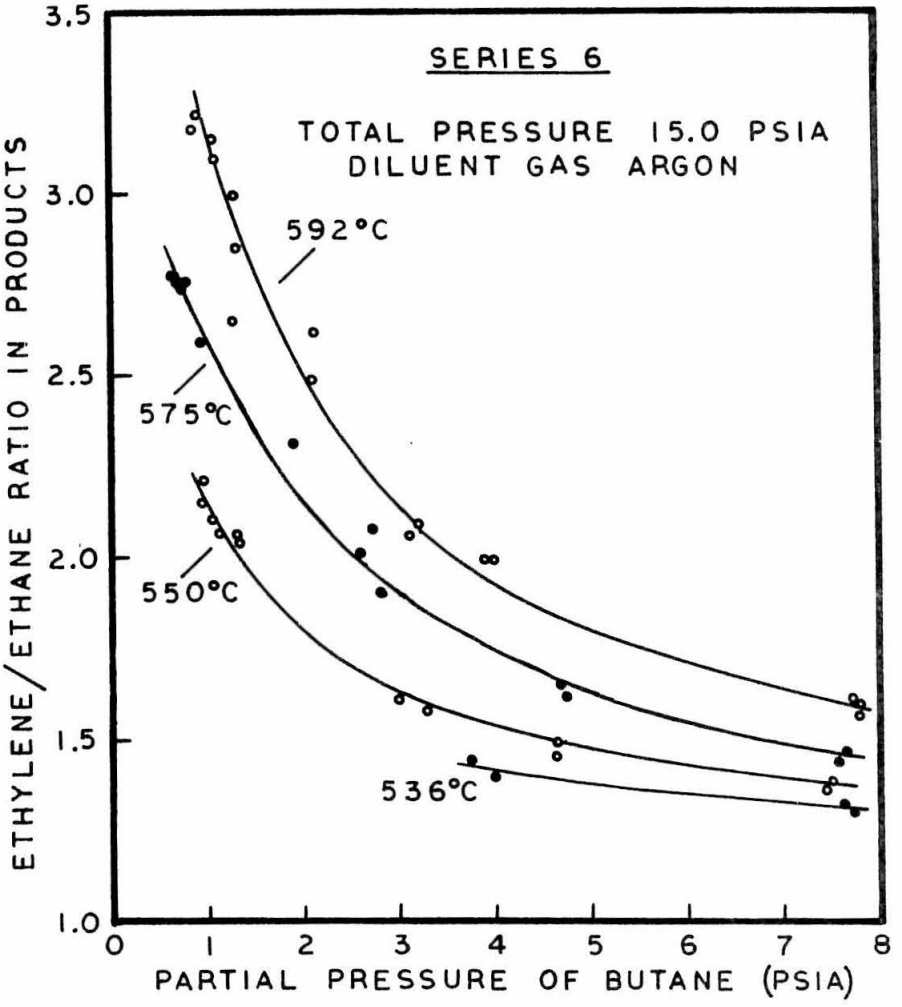


Figure 9. Variation in the ethylene/ethane ratio with temperature and pressure.

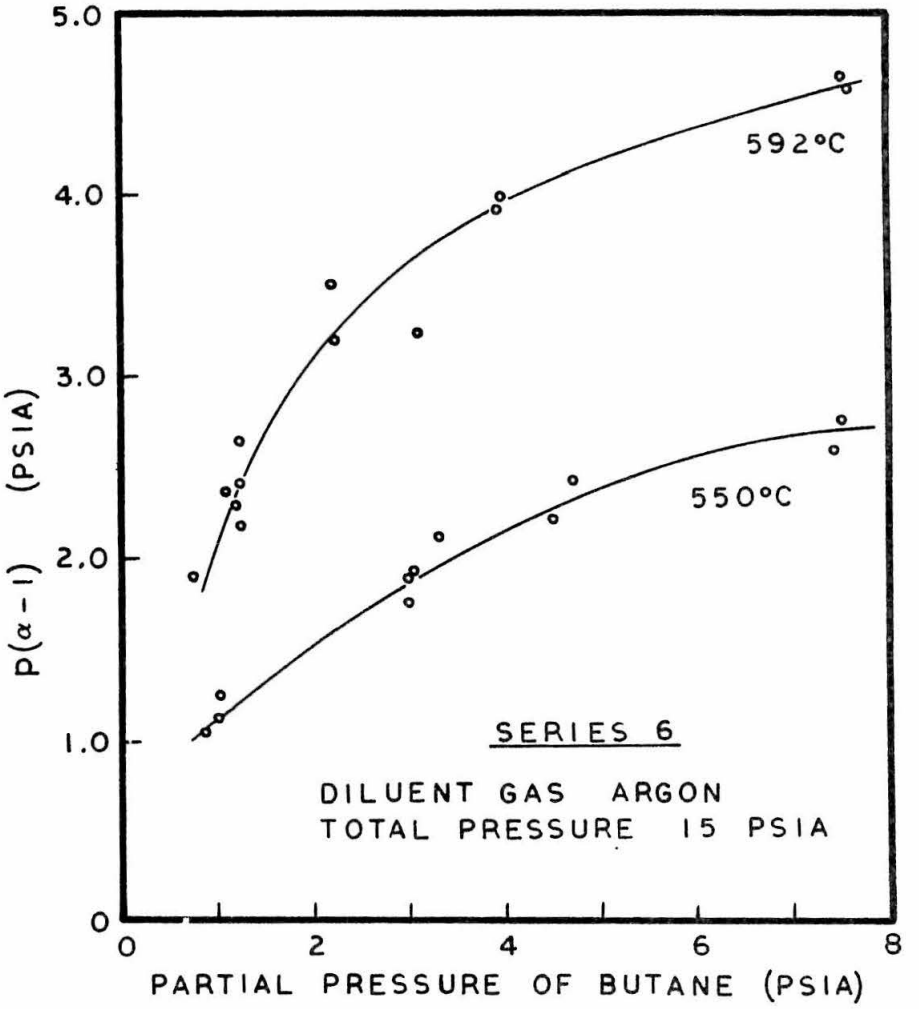


Figure 10. Plot of the function (α - 1)p against the partial pressure of n-butane.

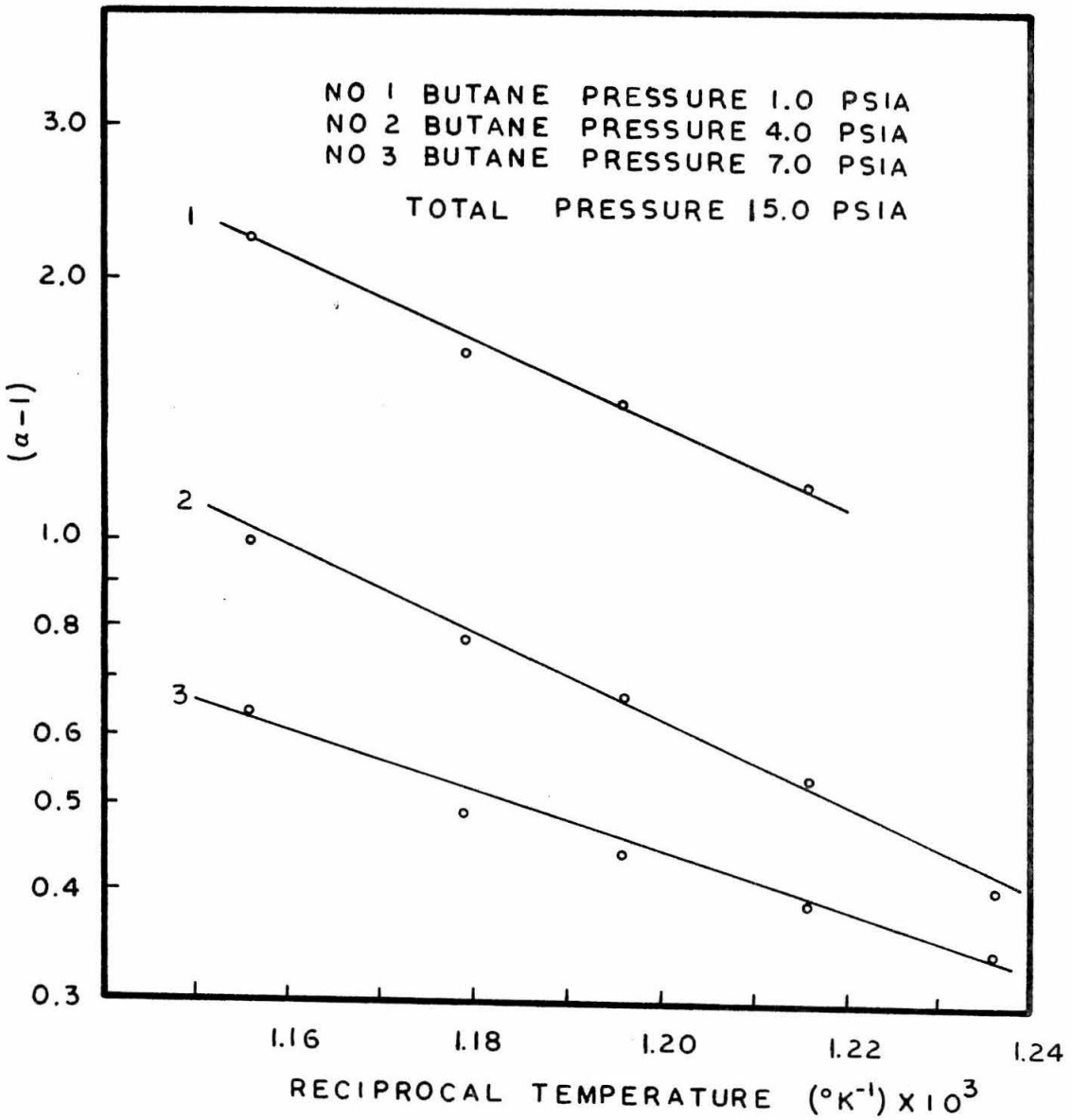


Figure 11. Plot of log (α - 1) against the reciprocal temperature.

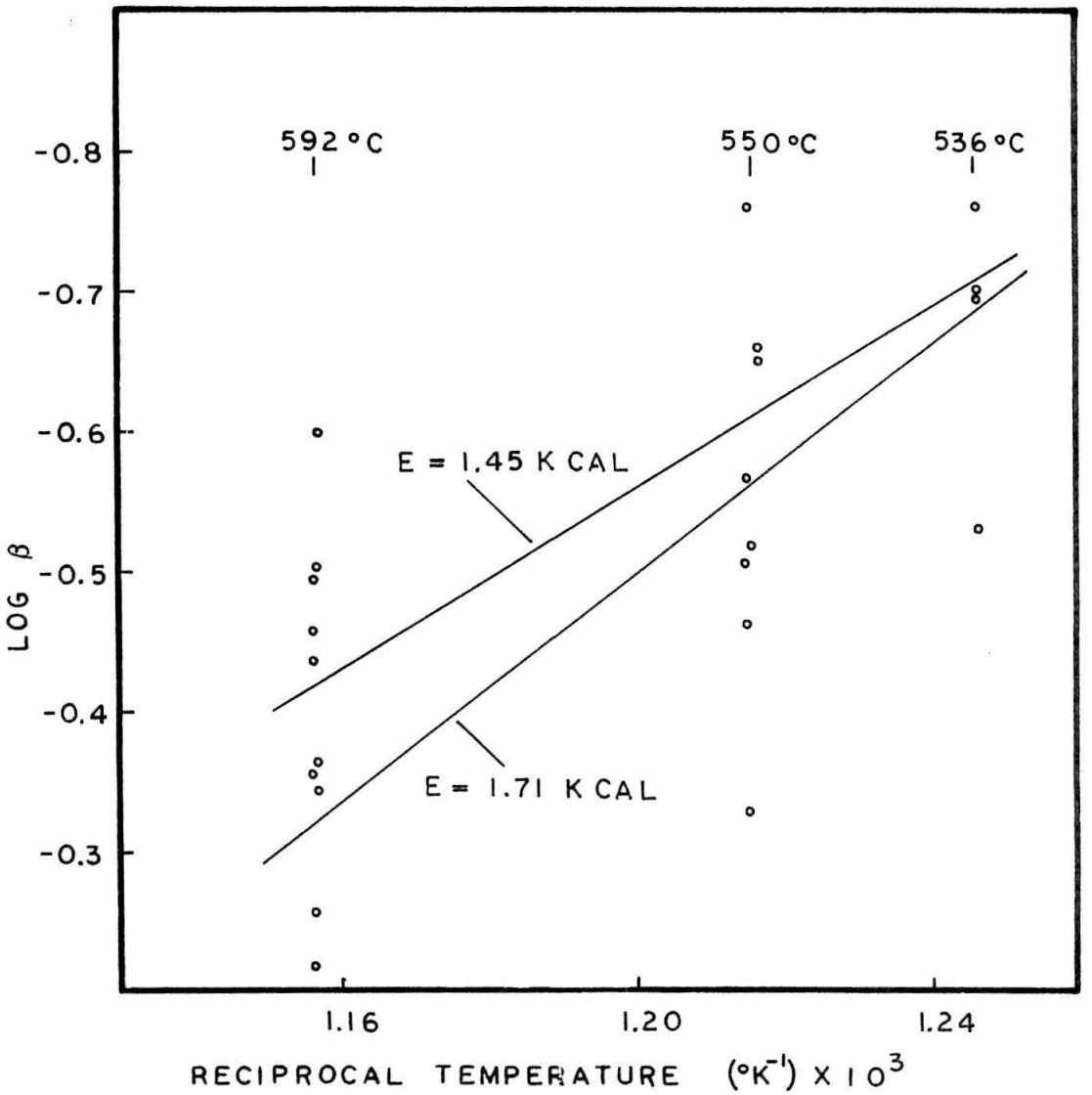


Figure 12. Plot of log α against the reciprocal temperature.

of 2.0 kcal./mole.

To this point the data were in good qualitative agreement with the data of Purnell and Quinn. This agreement indicated that the gold surfaces did not interfere to a serious extent with mechanism of the pyrolysis.

SERIES 7.

A point of immediate interest in these early stages of the work was to check the effects of varying the surface-to-volume ratio of the reactor as a further evidence of the homogeneity of the pyrolysis. For Series 7, a gold tube was packed with lengths of gold wire (of the same length as the tube) to give a surface-to-volume ratio of 165 $in.^{-1}$ as compared with the value of 64 $in.^{-1}$ for Series 6. The rate data taken using the packed reactor are shown in Figure 13. Figure 14 is an Arrhenius plot for the variation of the rate of reaction with temperature and includes data from Series 6.

The rate data for Series 6 and 7 differ by 11% throughout the entire range of conditions which were studied but otherwise have the same characteristics. Probably the 11% discrepancy was due to errors in the determinations of the reactor volumes. Both sets of data show a similar "break-off" effect and have similar trends in the conversion-time plots (Figure 8). It was unlikely that the phenomena which were responsible for the "break-off" and

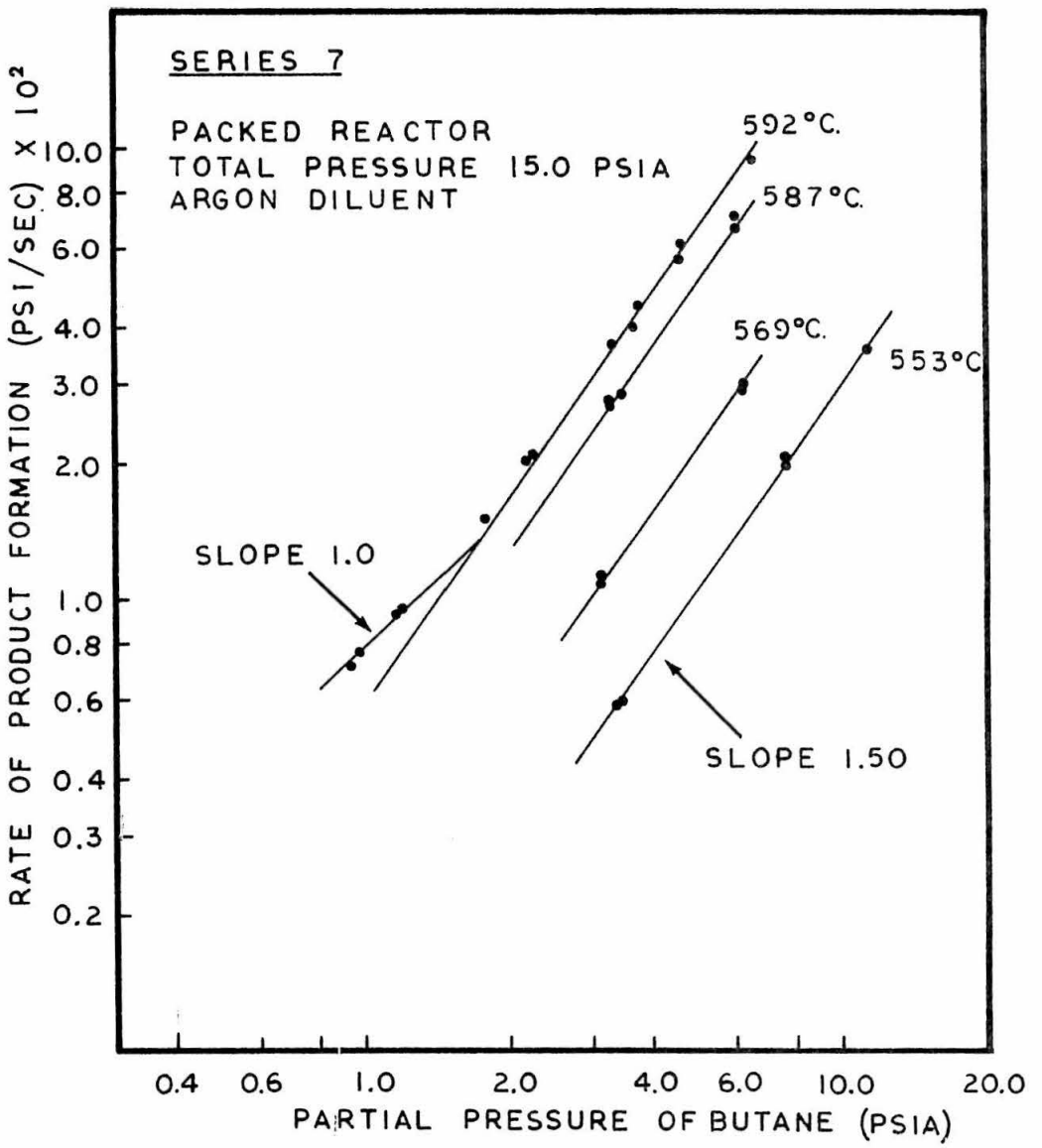


Figure 13. Rate - Pressure curves for the pyrolysis of n-Butane in the packed reactor.

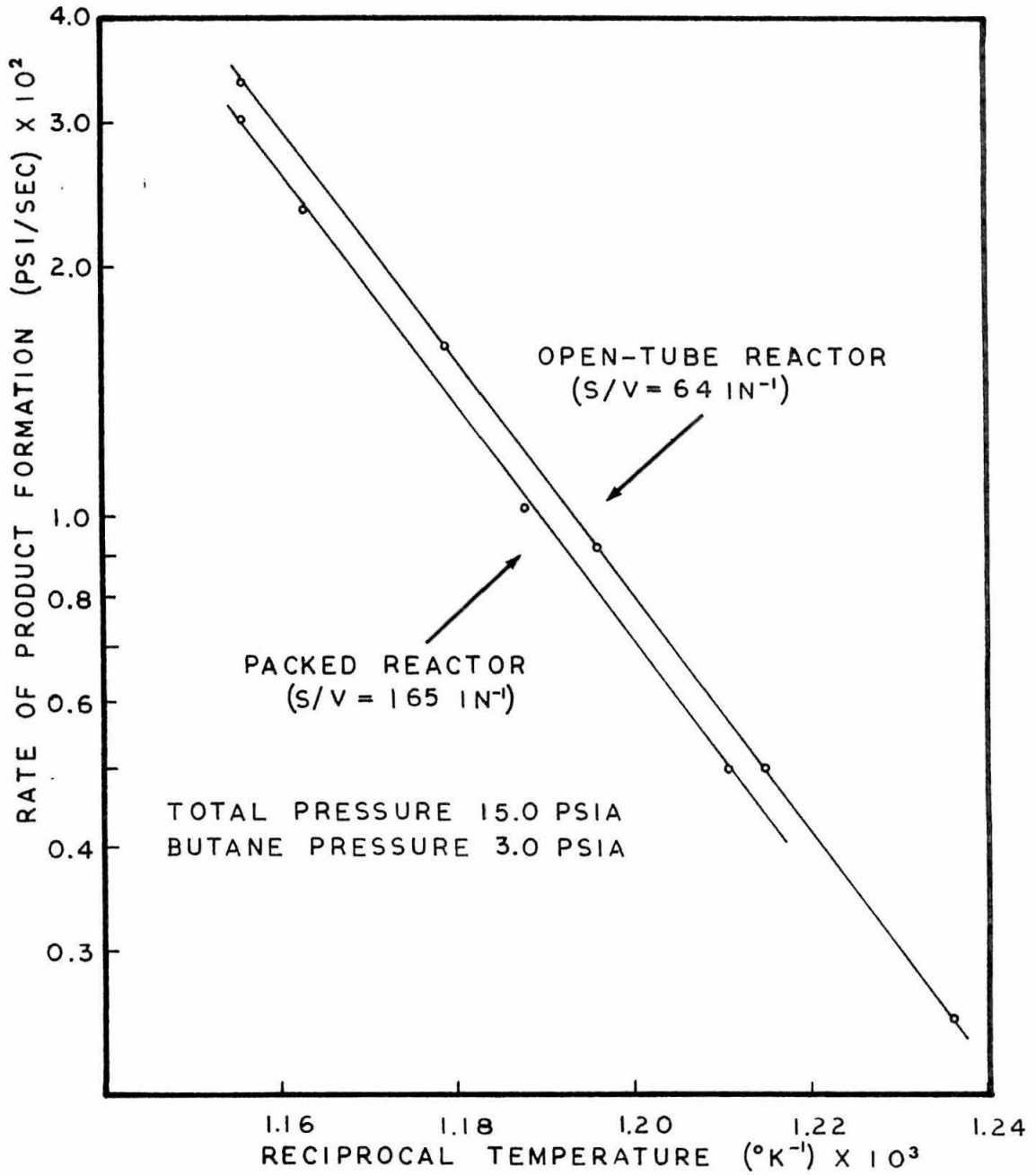


Figure 14. Arrhenius plots for the open-tube and packed reactors.

inhibition effects were markedly dependent on the surface-to-volume ratio.

In light of the highly non-linear effects of changes in the surface-to-volume ratio in many kinetic systems, the findings of Series 6 and 7 do not constitute a decisive demonstration of the homogeneity of the system. The term "surface effects" could refer to either the behavior of the gold surfaces or to the effects of the carbonaceous deposits. The tubular flow reactor could not be used to discriminate between these two possibilities. A further major limitation of the study was that with the small-bore reactor tube the surface-to-volume ratios were fairly high (64 $in.^{-1}$ and 165 $in.^{-1}$).

SERIES 8.

a. The influence of trace levels of oxygen.

The first runs in this Series were an attempt to determine the effects of low concentrations of oxygen on the pyrolysis. Trace amounts of oxygen were added to the argon diluent. In some preliminary runs with less than 100 ppm. of oxygen the overall rate of reaction was depressed considerably below that of the normal rate of pyrolysis. For example, with about 30 ppm. oxygen in the diluent stream the rate of decomposition was half that of the normal rate. Traces of oxygen also considerably affected the product distibution, such, that, compared with the pyrolysis, the

relative yields of ethylene and propylene were increased but the relative yield of ethane was reduced. Butenes were formed to an increasing extent when oxygen was present. These observations were in qualitative agreement with the results of Appelby et al (39). A serious complication arose in trying to estimate the amount of oxygen that actually entered the reactor because trace amounts of oxygen were undoubtedly adsorbed onto the hot stainless steel walls of the diluent preheating tube. The reproducibility of the data was poor and was probably related to changes in the surfaces of the reactor when they were exposed to hot oxygen, this point was to be checked further in Series 10. Before further examining the reaction system at low levels of oxygen a considerable number of runs were performed at much higher levels of oxygen (several percent O_2 in the diluent). The runs with higher levels of oxygen were more reproducible and were capable of a better quantitative analysis since the rate of consumption of oxygen could be more easily followed. With trace levels of oxygen, the oxygen was completely consumed in the first few milliseconds of reaction.

b. Partial oxidation at high levels of oxygen.

The remaining runs were taken within the ranges of conditions indicated below:

Temperature: 458 to 566°C.

Partial pressure of butane: 3.5 to 16 psia.

Contact time: 0.4 to 2.4 sec.

Oxygen levels in the diluent: 1.0, 4.0, and 8.0%

Within the considerable encompass of these runs it was possible to draw up the general characteristics of the partial oxidation system although the data could not be reduced to a simple kinetic form. A restriction on the conclusions drawn from these runs should be noted; namely that with the chromatographic equipment developed for the pyrolysis studies it was not possible to conduct complete analyses of all the products of partial oxidation. It was not until relatively late in the Series that a suitable column was developed for the detection of carbon dioxide - an unexpectedly important product. Positive tests (silver-mirror) for aldehydes were also established. A complete analysis of products would require at least one more chromatographic column for the separation of the partially oxygenated products species. This omission does not invalidate the results which were obtained, but it does preclude a complete mechanistic and kinetic analysis. Most of the partial oxidation work was performed between 458 and 504°C. A number of runs were also carried out at 566°C. where both pyrolytic and partial oxidation processes were evident. The high temperature work is most easily discussed first.

1. Partial oxidation at 566°C. and high oxygen levels.

Because of the rapid rate of removal of oxygen at this temperature, the reactor operated as an integral conversion unit on the oxygen. Conventional kinetic studies of the rate of removal of oxygen could not be made without using extremely high flowrates of gas through the reactor.

Figures 14 and 15 show the variation in the yields of various products with the contact time for 1.0 and 4.0% oxygen in the diluent gas. Under these conditions butenes were a major proportion of the total products and the rates at which these components were formed were extremely high in the initial stages of the reaction. The shape of the yield-time curves for the butenes can be best explained if the butenes, as initial products of the reaction, were rapidly attacked by oxygen, as proposed by Knox (40). The levelling-off in the curves corresponded to complete conversion of the oxygen. The cracked products probably resulted from the normal mechanism of pyrolysis although the initial distribution of cracked products was strongly influenced by the presence of oxygen. The concave shape of the curve for ethane (Figure 14) is especially interesting in that it shows the inhibitory role of oxygen on ethane formation.

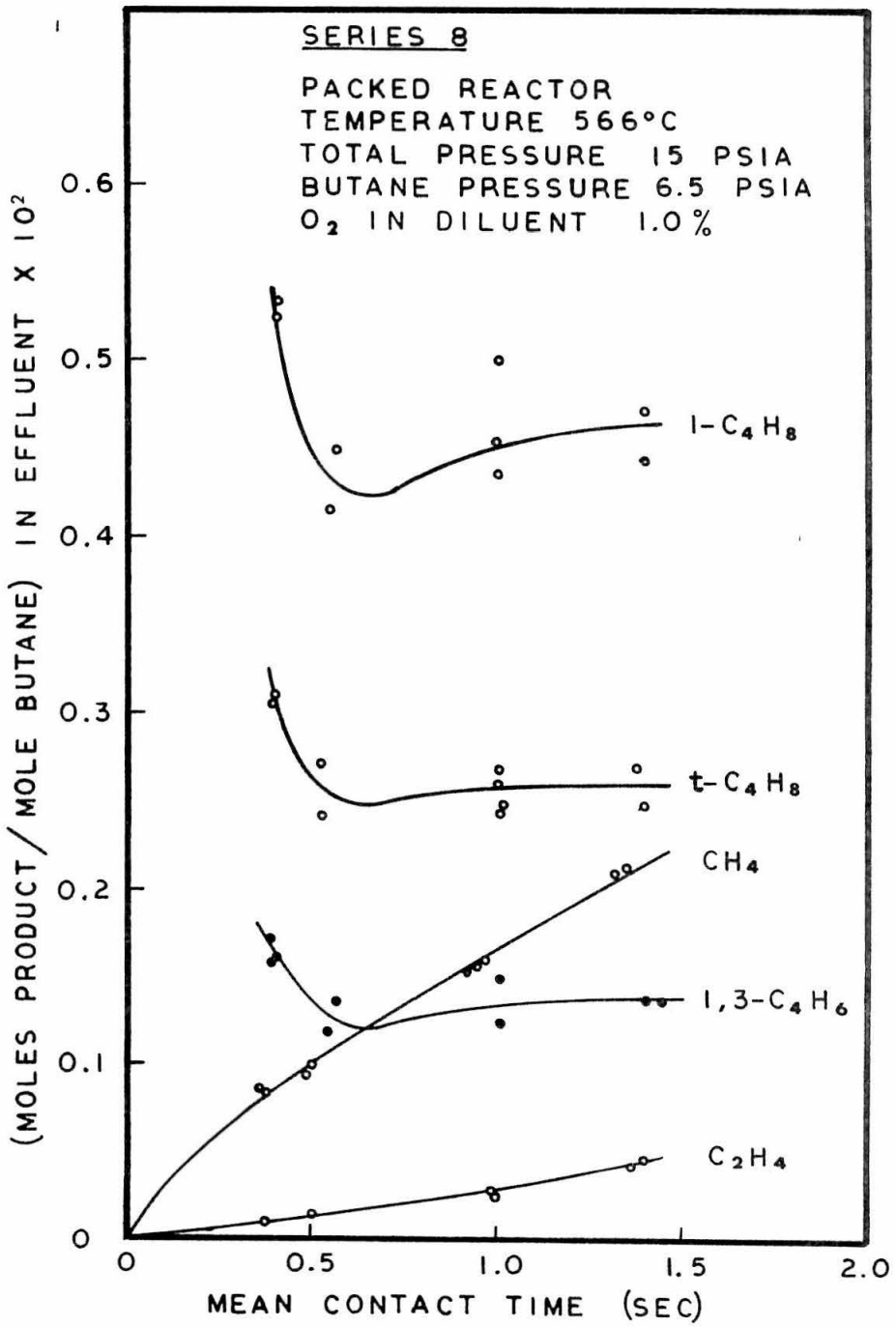


Figure 14. Plot of the yield of products against the contact time - high temperature partial oxidation.

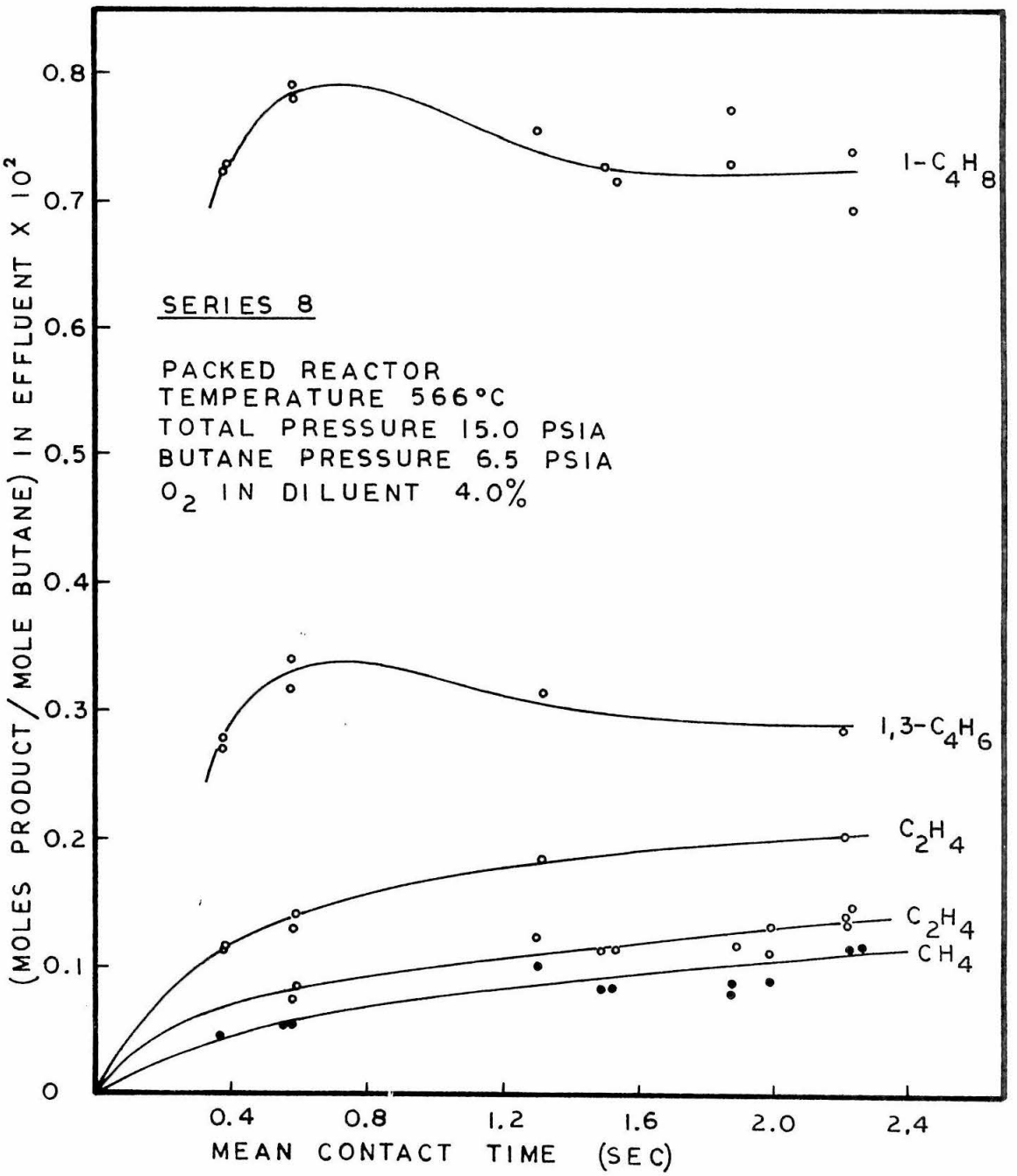


Figure 15. Plot of the yield of products against the contact time - high temperature partial oxidation.

2. Partial oxidation studies at low temperatures.

The temperature range for this Series of runs was 458 to 504°C. and was the lowest range in which measurable rates of reaction occurred. Under these conditions the formation of cracked products was comparatively negligible.

Figures 16, 17 and 18 summarise the data on the yields of 1-butene and of 1,3-butadiene as functions of the mean contact time. The data for both cis- and trans-2-butene showed similar characteristics to the other olefins. Two features of the curves may be noted:

a. The levelling-off of each curve corresponded to complete conversion of the oxygen. The fact that the curves came to levels which increased with temperature would indicate the relative temperature dependencies involved in the sequence:

Butane ⟶ Butenes ⟶ Carbonyls etc.

b. Figures 17 and 18 show that the yields of products were relatively independent of the oxygen level between 1 and 8% oxygen in the diluent. This surprising result checks well with the work of Steitz et al (68) though it is in disagreement with the findings of Appelby et al (39).

The rate of consumption of oxygen was not easily correlated. Figure 19 is a plot of the square root of the oxygen concentration in the effluent against the contact time; the relationship should be linear for a system which is

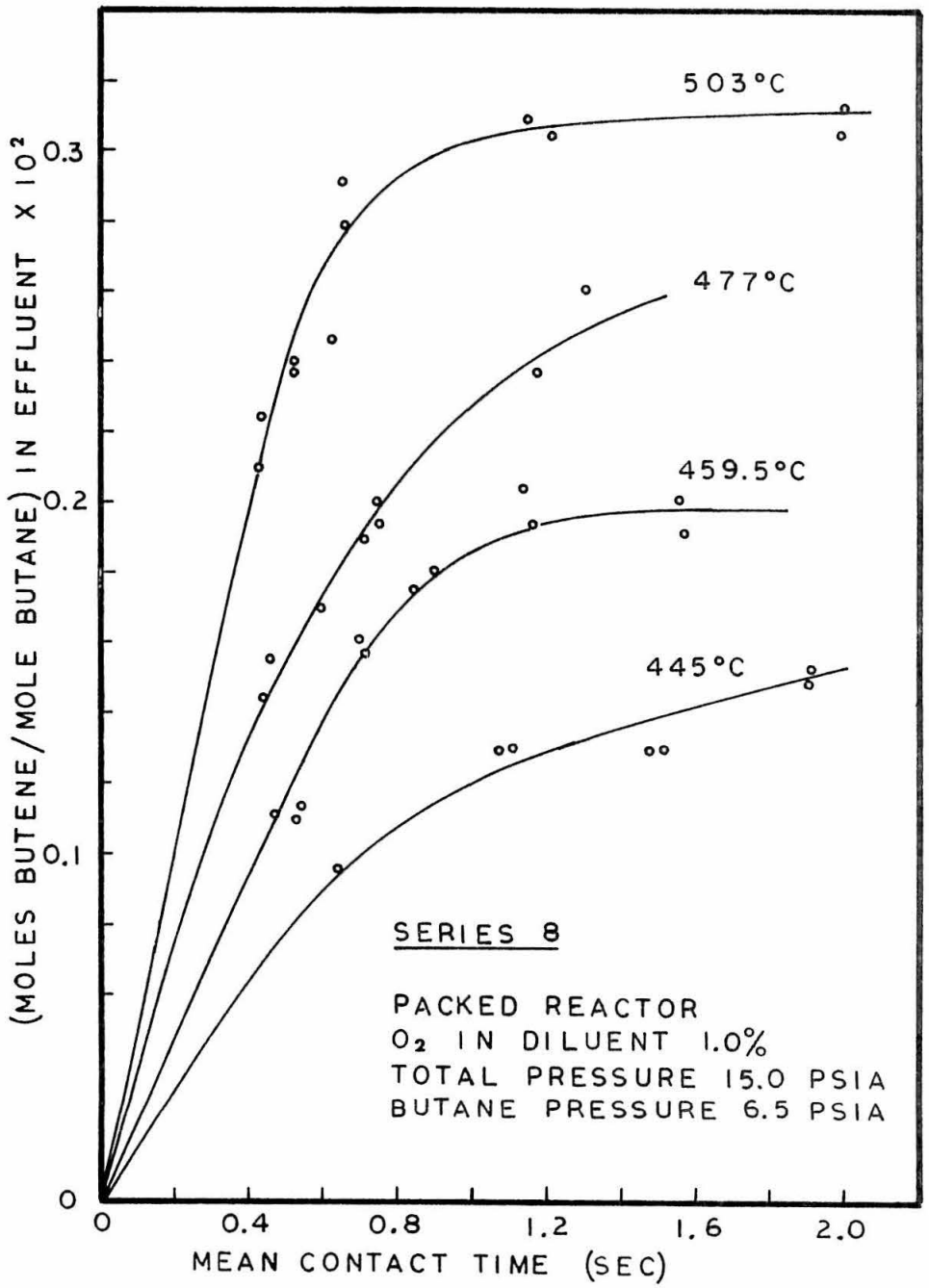


Figure 16. Plot of the yield of 1-butene against the contact time.

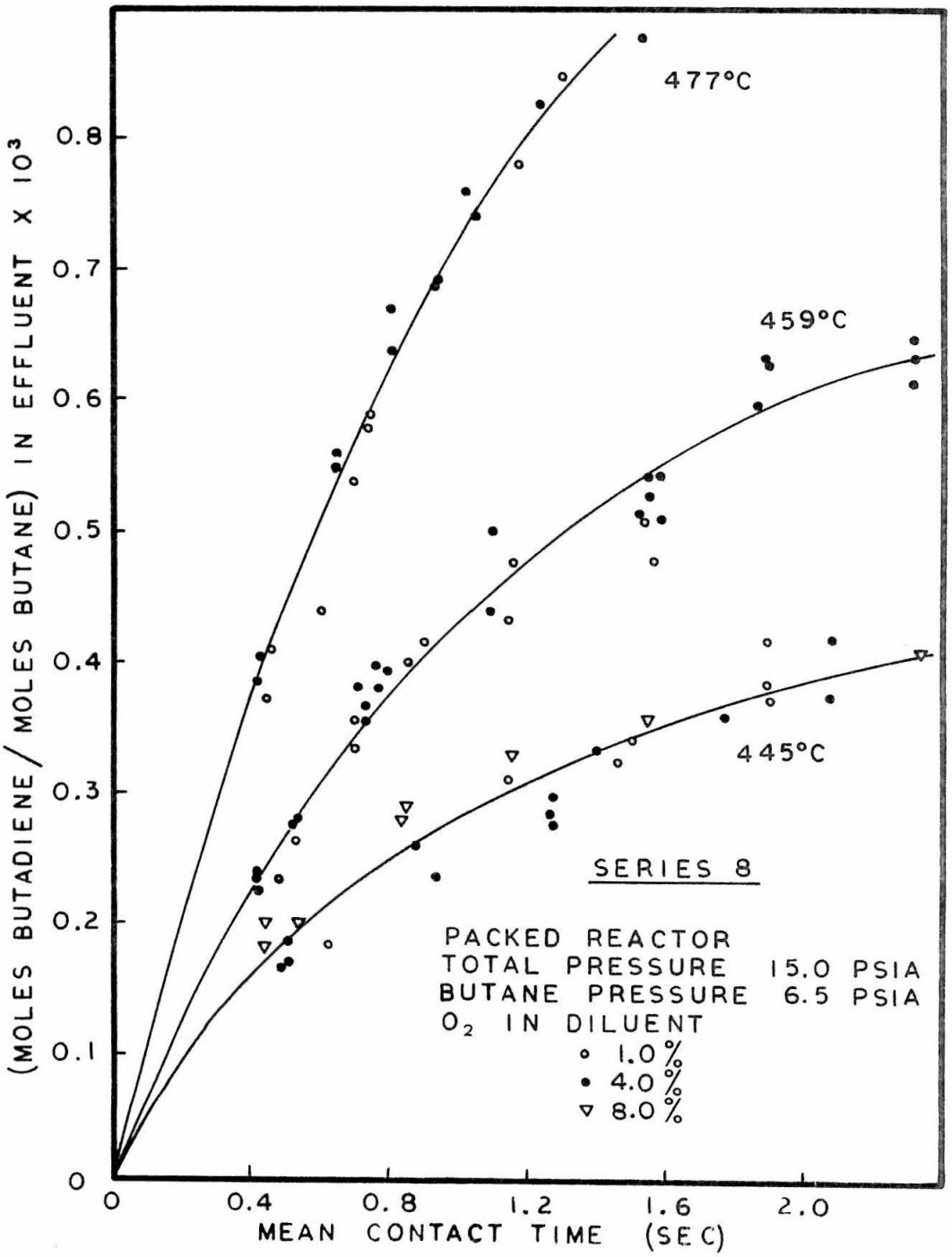


Figure 17. Plot of the yield of 1,3-butadiene against contact time for several levels of oxygen.

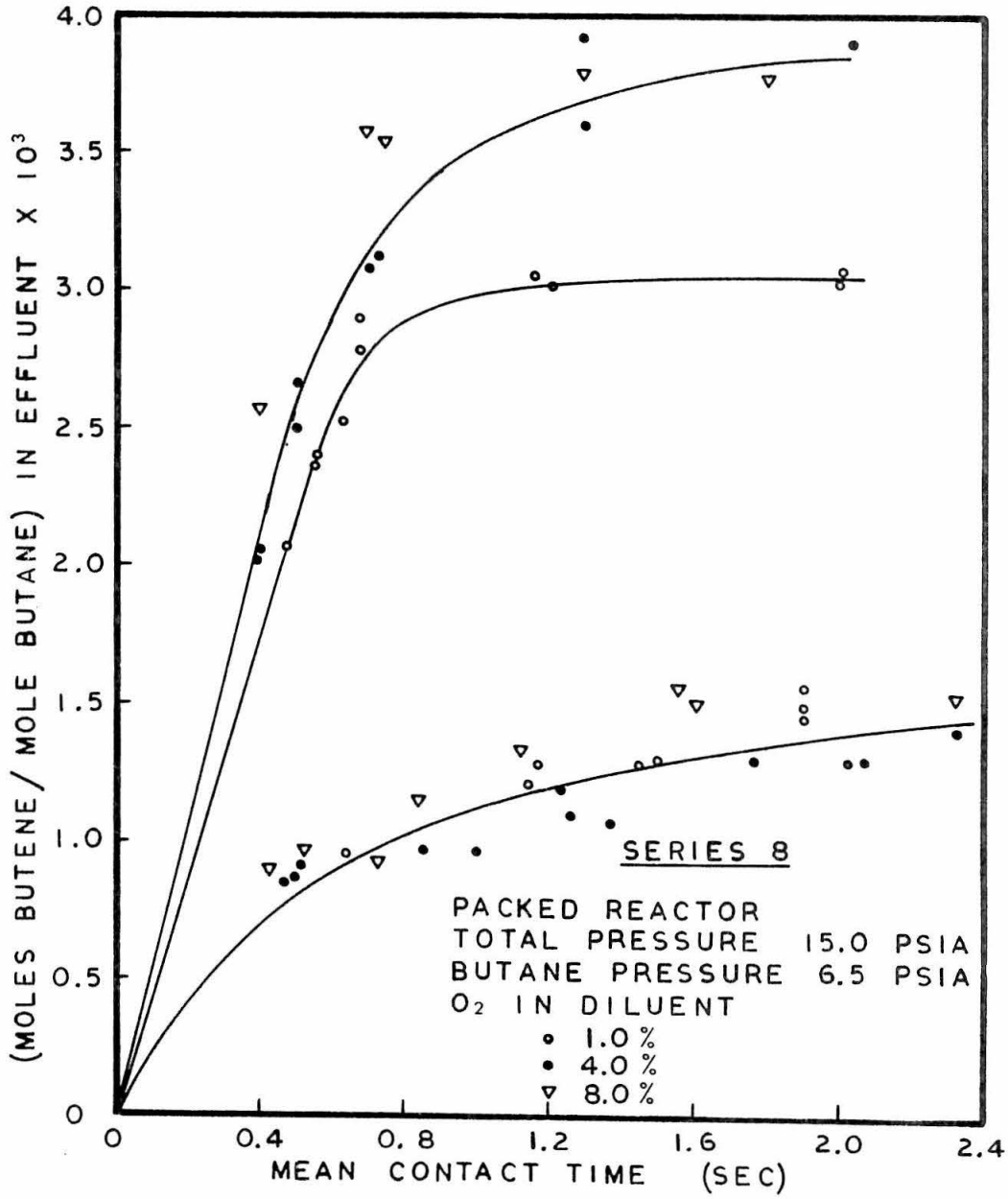


Figure 18. Plot of the yield of 1-butene against contact time with several levels of oxygen.

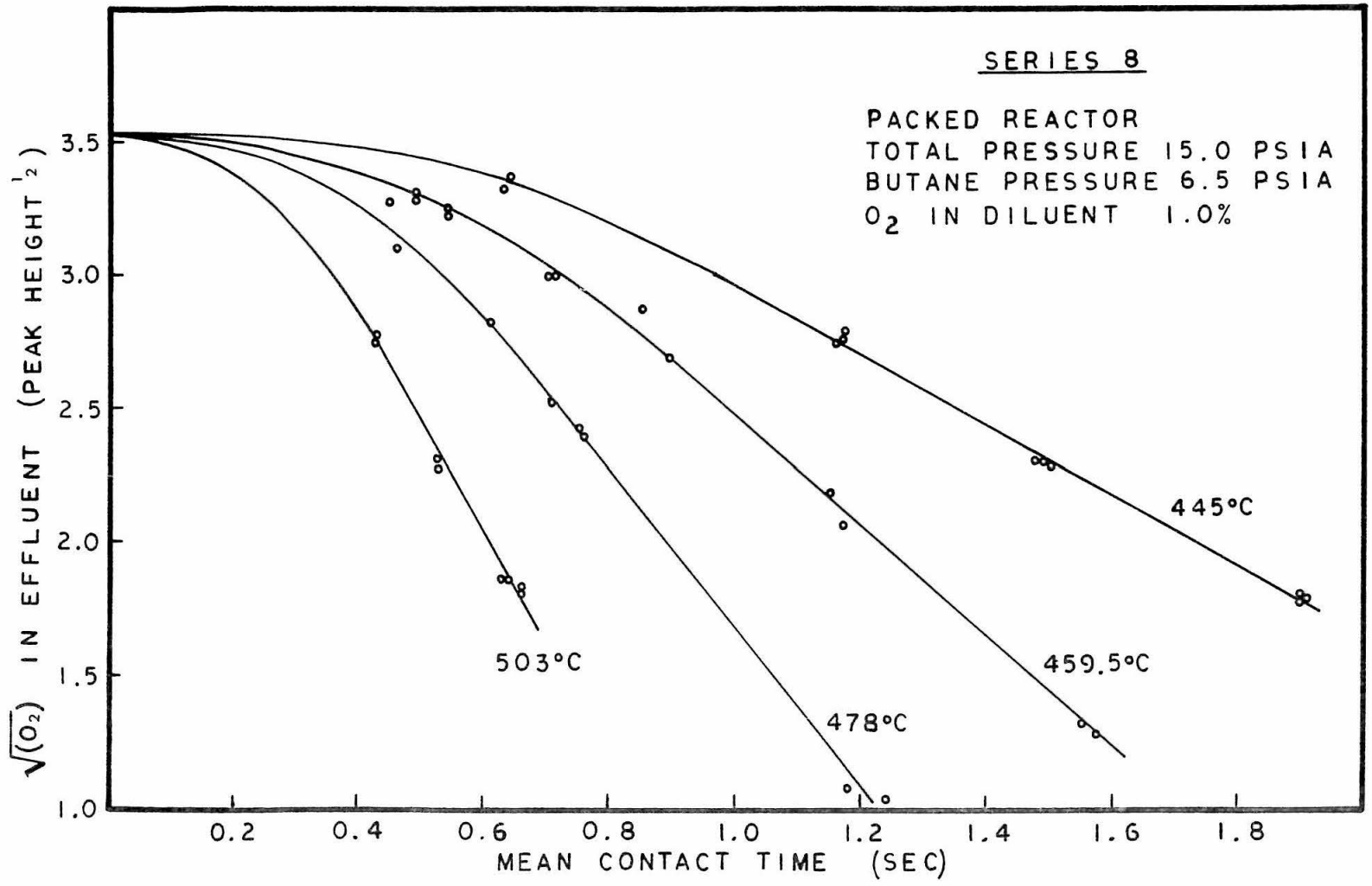


Figure 19. Consumption curve for oxygen, plotting the square root of the concentration of oxygen in the effluent against contact time.

half-order with respect to the oxygen. No other correlations proved satisfactory. The slopes of the linear portions of Figure 19 could not be fitted with an Arrhenius-type of plot. A plot of the percentage of oxygen consumed against the contact time would be S-shaped, an induction effect being typical of partial oxidation systems. The formation of the initial products of the reaction (the butenes) is not accompanied by any significant induction period. The difference between the consumption curves for the oxygen and the butane indicates that the major uptake of oxygen was due to the butene and subsequent products in the oxidation.

An attempt was made to determine the influence of the partial pressure of the butane on the kinetics of partial oxidation (Runs 136 to 160a). The initial rate of reaction was approximated by an extrapolation of the mean rate of reaction back to zero contact time. This extrapolation could only be performed very crudely because of the highly non-linear nature of the yield-time curves. Figure 20 is a plot of the estimated initial rate of reaction against the partial pressure of butane; the plot has a slope of about 0.8. These runs were performed at various total pressures in order to maintain a constant diluent (and oxygen) pressure. The effect of varying the diluent pressure was not studied, though Steitz et al (68) noted only minor effects on changing the diluent (nitrogen) pressure.

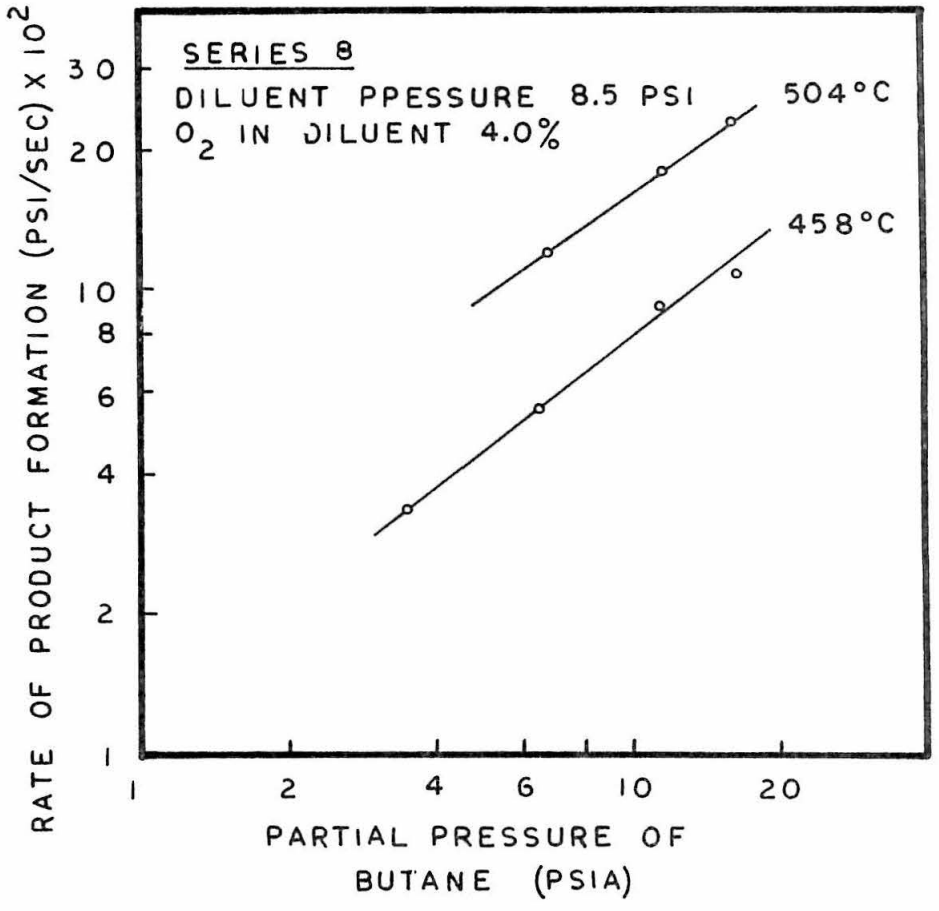


Figure 20. Plot of the initial rate of reaction against the partial pressure of butane - low temperature partial oxidation.

Using the initial rates of reaction which could be estimated from Figures 16 and 17 an Arrhenius plot was drawn up (Figure 21). The validity of an Arrhenius plot for a complex reaction is probably fortuitous, nevertheless the data could be satisfactorily correlated with an activation energy of about 25 kcal./mole.

It was not until fairly late in the Series that tests for carbon dioxide were conducted using a chromatographic separation over Poropak Q. Surprisingly large amounts of carbon dioxide were formed. Data taken at 566°C. (Runs 190 to 193) showed that the level of carbon dioxide was constant at contact times above 0.4 seconds. After initiation of the decomposition a rapid chain-branching sequence must have been set up to account for the high yields of carbon dioxide at short contact times. Figure 22 is an Arrhenius plot of the initial rate of formation of carbon dioxide; an activation energy of 29 kcal./mole was estimated. At various points throughout the Series, tests had been performed for carbon monoxide and invariably showed very low levels of the monoxide. The carbon dioxide was probably not caused by oxidation of the monoxide (63). Other than the temperature the factors associated with the formation of carbon dioxide were not studied systematically. Due to an oversight in the calibration of the CO_2 detector the levels of CO_2 are only reported on a relative basis.

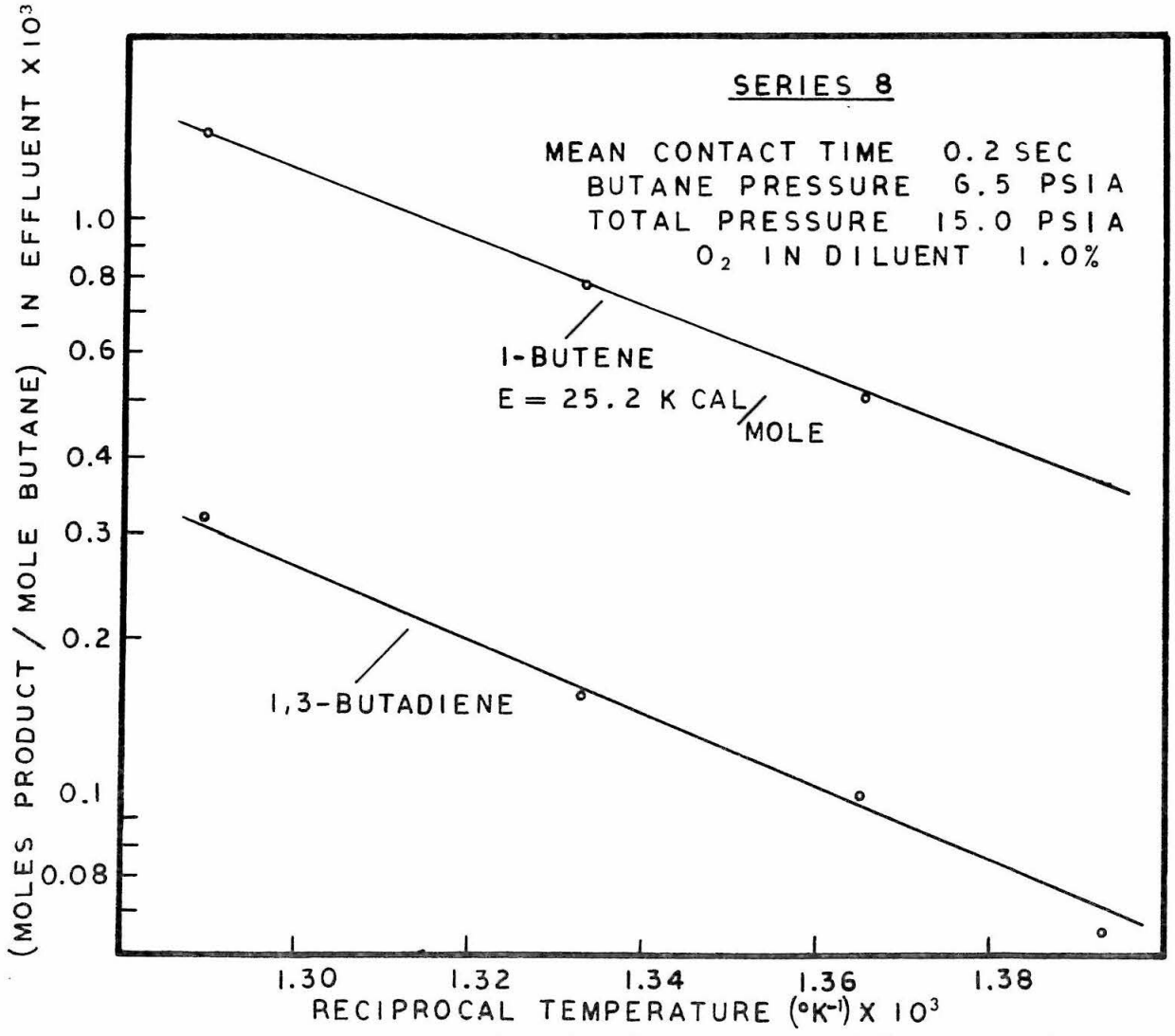


Figure 21. Arrhenius plots for the formation of 1-butene and 1,3-butadiene.

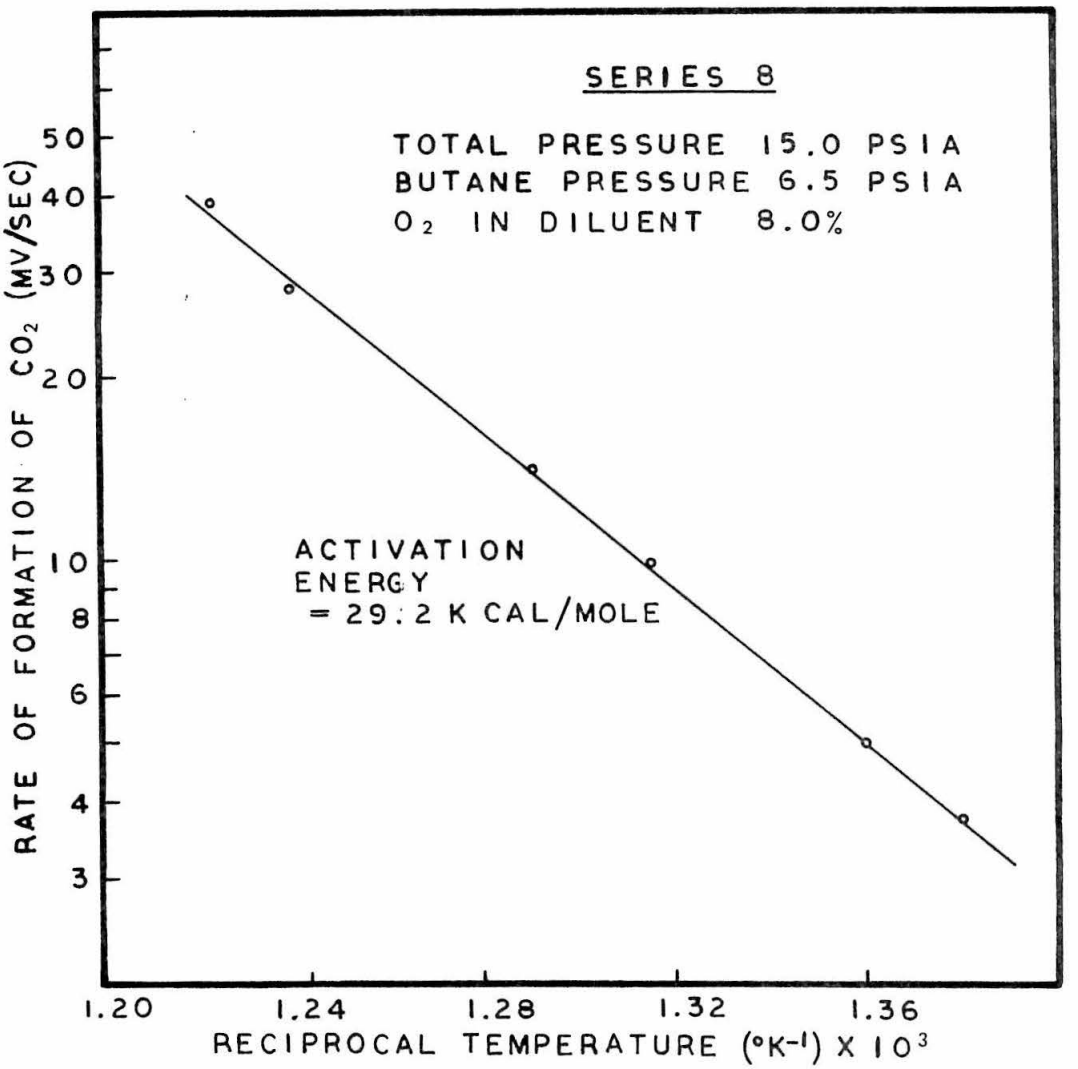


Figure 22. Arrhenius plot of the rate of formation of carbon dioxide.

c. Further runs at low levels of oxygen.

Following the above partial oxidation studies attempts were made again to study the reaction with oxygen levels in the 5 to 100 ppm. range. Again the studies were complicated by the impossibility of reliably intoducing low levels of oxygen into the reactor.

Oxygen traps were then installed in the feed lines and a number of pyrolysis runs were performed. The rates of decomposition in these runs were much lower than those of Series 7 (by a factor of about 2.5). The product compositions in the two cases were comparable. At this stage of the study the only conclusion which could be drawn about the shift in the rate was that the introduction of hot oxygen into the reactor system had caused some irreversible change in the system. The most likely explanation of the shift would be in terms of some surface effect. A more systematic study of the variation in the rate of pyrolysis in reactors which were subjected to various chemical treatments was then undertaken in Series 9.

SERIES 9.

The purpose of this Series was to demonstrate the effects on the pyrolysis of various chemical treatments of the reactor tube. The open-tube reactor which had been used in Series 6 was used for this Series. This reactor had not been previously exposed to hot oxygen. A preliminary

start-up check (Run 6) checked well with the results of Series 6. The reactor was then exposed to hot oxygen for several hours. Following the oxygen treatment the reactor system was purged free of oxygen using the diluent and quench streams. A further start-up test was then performed (Run 7). Subsequent runs used different durations of oxygen treatment. The results of all of the runs are summarised on Figures 23 and 24 for the yields of methane and ethane respectively. The other major products of the pyrolysis, ethylene and propylene, showed behavior similar to that of ethane. The yield of hydrogen increased continuously with running time. The results for Runs 7 through 13 fall within a band of considerable spread but show no obvious correlation between the behavior of a run and the duration of pretreatment with oxygen. At the end of each run the reactor was re-treated with oxygen. Traces of carbon dioxide could be detected in the effluent for upto 2 hours after the oxygen was admitted to the reactor.

A further group of runs (Runs 14 through 18) was carried out in which oxygen treatment was followed by hydrogen treatment, after which the pyrolysis was run as usual. Again the results showed no systematic variation with the duration of treatment with hydrogen, (Figures 25 and 26). The curves for the oxygen-hydrogen treated reactor showed significantly different trends from those of the oxygen treated reactor. Runs 17 and 18 were check

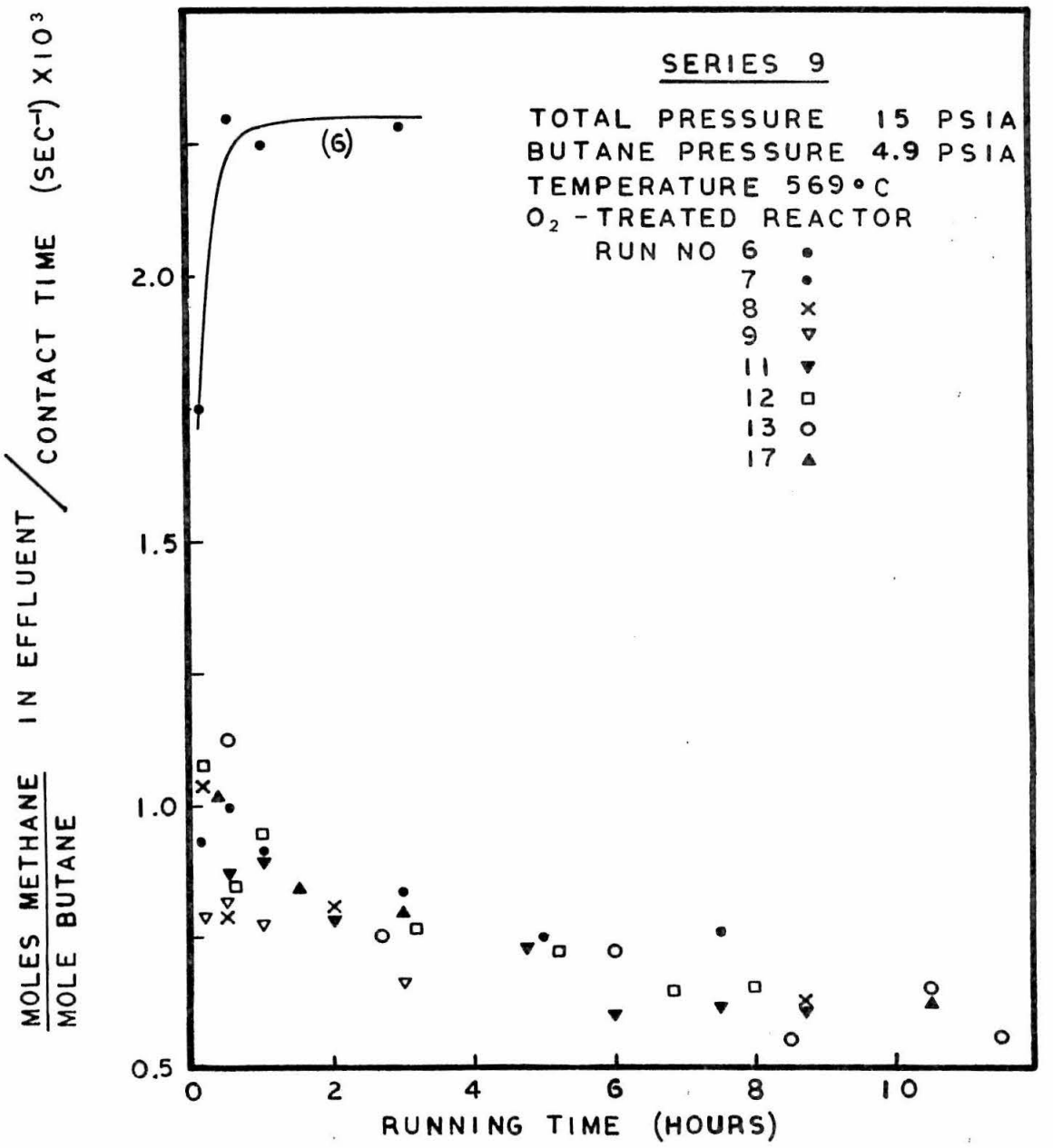


Figure 23. Rate of formation of methane against running time for an oxygen treated reactor.

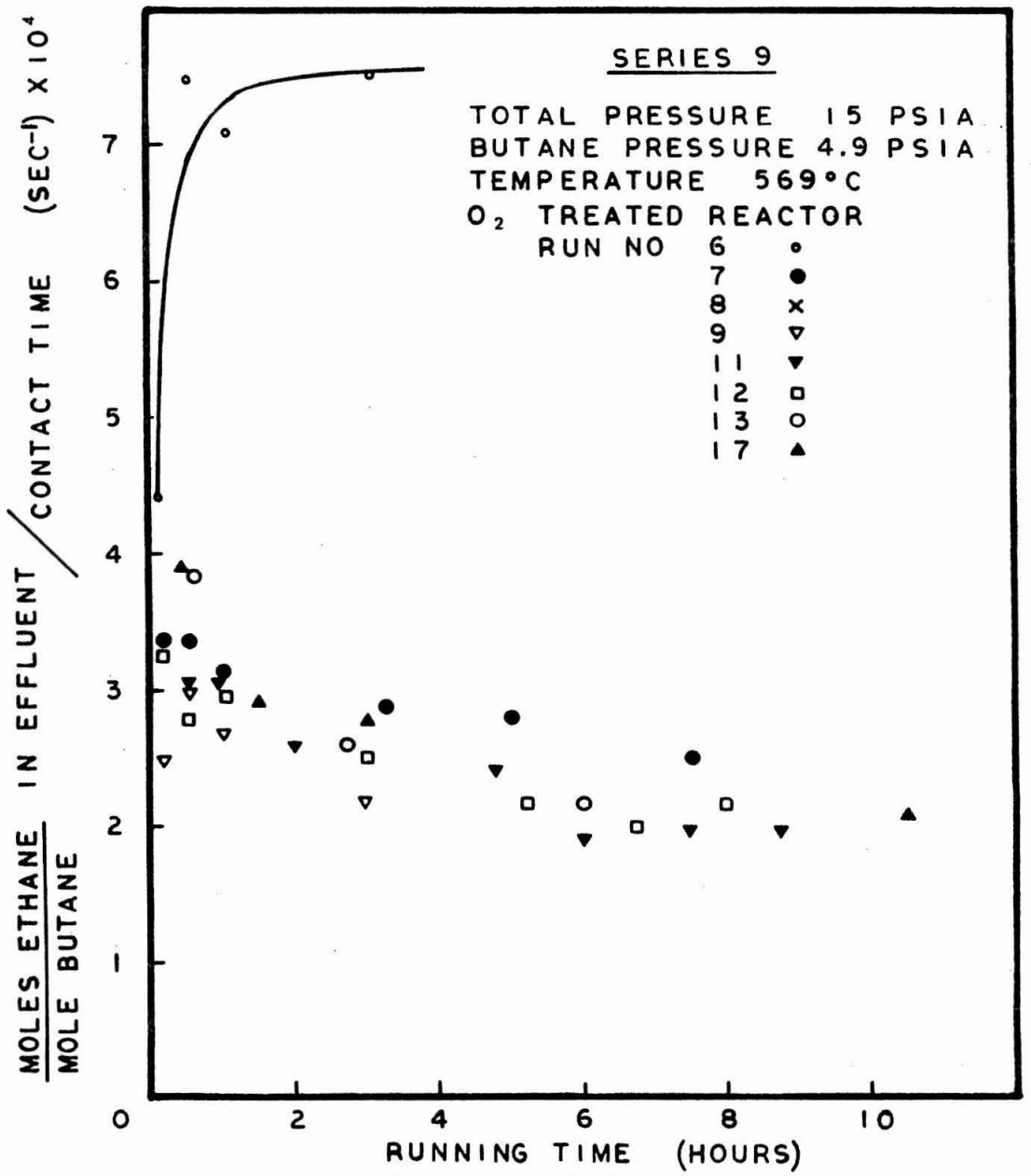


Figure 24. Rate of formation of ethane against running time for an oxygen treated reactor.

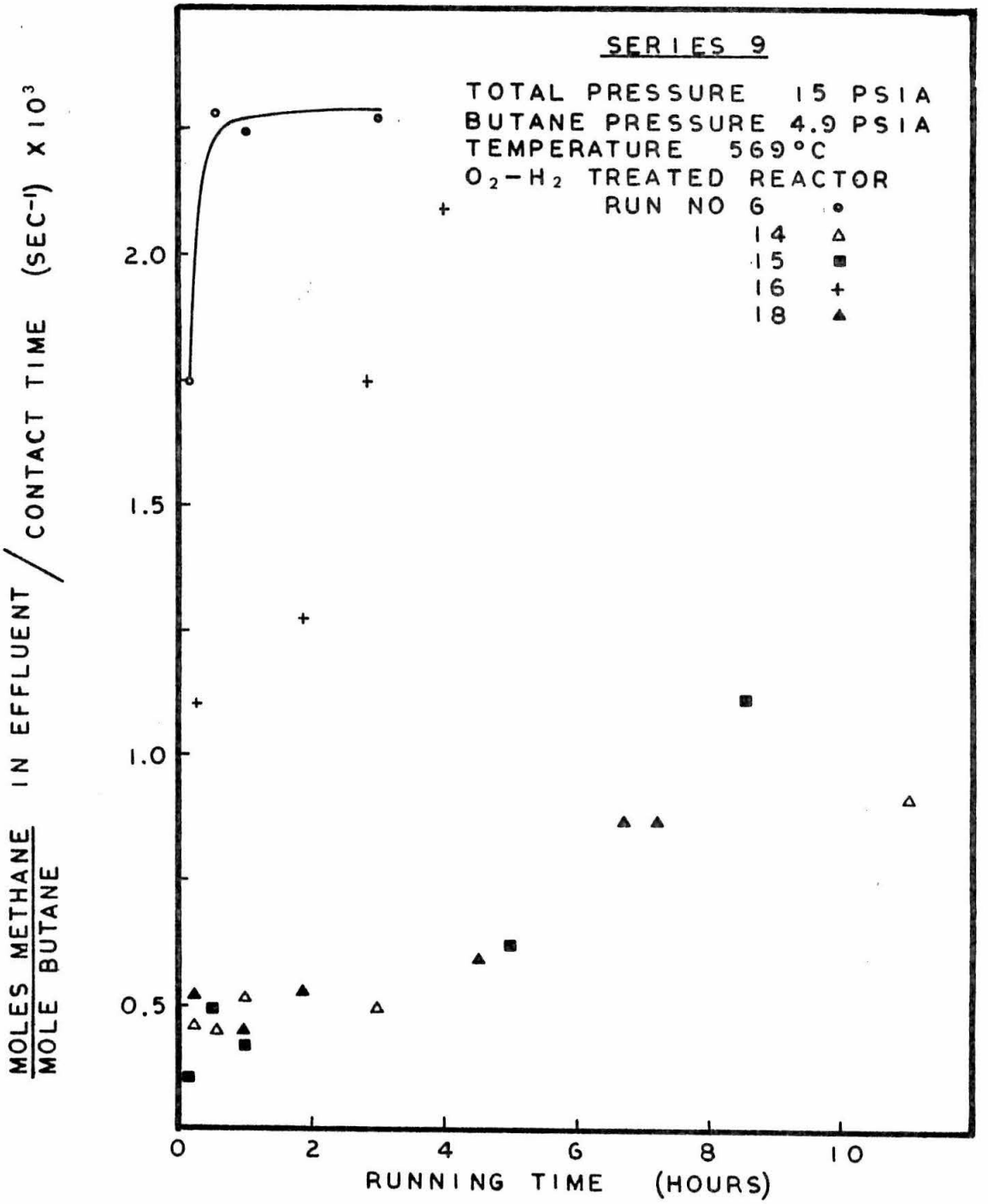


Figure 25. Rate of formation of methane for an oxygen-hydrogen treated reactor against running time.

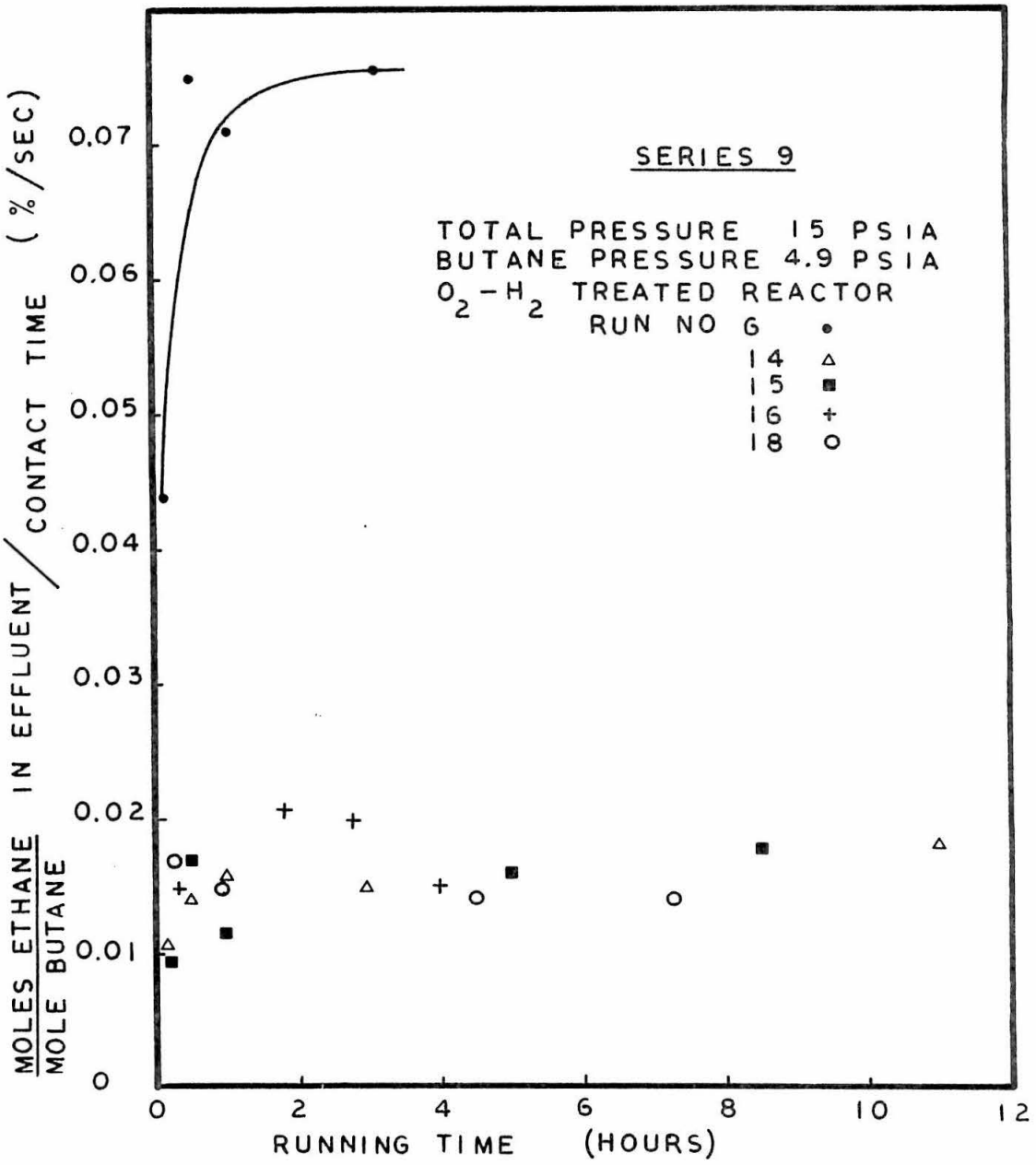


Figure 26. Rate of formation of ethane against running time for an oxygen-hydrogen treated reactor.

runs which indicated that the reactor behavior following both types of treatment could be reproduced. In most of the runs the product distribution at start-up was similar to that observed in Series 6. With increased running time the yield of product showed a complex behavior which depended on whether the reactor was oxygen or oxygen-hydrogen treated. With increased running time the fractional yield of methane in the products increased, slowly for an oxygen treated reactor and rapidly for an oxygen-hydrogen treated reactor. For all runs the yield of hydrogen increased continuously with running time. These observations imply that the hydrogen-to-carbon ratio increased with running time; this finding constitutes indirect evidence for the formation of carbonaceous deposits within the reactor.

The variation in the rates of reaction with the various pre-treatment operations indicates, almost certainly, that surface effects are complicating the normal mechanism of pyrolysis. A plausible factor which could explain the results involves contamination of the gold surface by impurities. Two sources of impurities are possible:

a. The diluent and quench gases contact hot stainless steel surfaces in their passage to the reactor. These gas streams could carry small particles of surface scale from the steel surfaces into the reactor. If

however this were the major source of contamination it would be difficult to explain the extremely stable runs of Series 6 and 7 and to explain why Run 6 of Series 9 checked closely with the earlier results.

b. Another source of impurity on the gold surfaces would be due to the original oxidizable impurities in the gold. The gold tubing used in these studies was "pure" grade (99.99% gold) so that, at the ppm. level, traces of copper, silver and iron were present. These are all oxidisable impurities and the resulting oxides could be reduced by hydrogen. The effect of blowing oxygen through a tube of impure gold would be to bring the impurities to the surface forming a layer of oxides. A typical lot sample of the gold used in the micro-reactor would contain about 20 ppm. each of copper, silver and iron (Wilkinson Co.). Some contamination of the gold surfaces was almost inevitable, particularly in light of the work of Plumb and Thakkar (69).

Whilst looking into the problem of the purity of the gold a very simple method was used to give a qualitative test for the purity. By holding a sample of the gold in a hot, oxidising flame for several minutes, the formation of a discoloring coating indicated that substantial traces of

impurity were present. If the gold surfaces remained clean and bright then the impurity levels were probably below 100 ppm..

Because the results of Plumb and Thakkar were a likely explanation for the spurious effects noted in the pyrolysis, the next step was to find a suitable means of removing the oxide layers. Treatment of the surfaces with dilute acid was one obvious possibility. To eliminate the contamination effect due to scale from the stainless steel surfaces an all-gold reactor was designed in which all streams of hot gas contacted gold surfaces only. The all-gold reactor could be acid-treated in situ and was put into operation for the next series.

SERIES 10.

The aim of this Series was to examine the behavior of an all-gold reactor the surfaces of which could be subjected to various chemical treatments. The following sequence was adopted:

1. A start-up test was performed on the all-gold reactor as assembled (with no chemical treatment). The results for this Run (No. 1) are indicated on Figure 28.
2. Continuing on from the start-up test a set of runs was carried out with the untreated reactor to determine the rate of pyrolysis as a function of temperature and pressure.

These results are summarised on Figure 27 and show very similar trends to the results obtained in Series 6. However the rate data for the all-gold system were consistently lower than those for its predecessor. The decrease implied that the presence of a hot stainless steel surface in the diluent line could influence the kinetic behavior in the main reactor tube, presumably by the carry-over of surface scale from the preheat tube.

Interestingly enough, Figure 27 shows that the "break-off" effect may result from the establishing of a half-order effect rather than the first-order effect which was tentatively proposed in Series 6. A shift from three halves-order to half-order can be predicted from a steady-state analysis of the homogeneous pyrolysis of n-butane. Further study of the "break-off" effect was made in Series 12 and 13.

3. All further runs were start-up tests of reactors which had been subjected to either treatment by hot oxygen or by a treatment of hot oxygen followed by a nitric acid etch. Some of these results are summarised on Figures 28 and 29. The effects of hot oxygen treatment and of oxygen treatment followed by an acid etch were studied separately. The etching solution (30% nitric acid) was always followed by repeat washings with triple-distilled water.

After the first acid etch treatment was completed no further change took place in the asymptotic rate of pyrolysis (at large running times). Within the limits of experi-

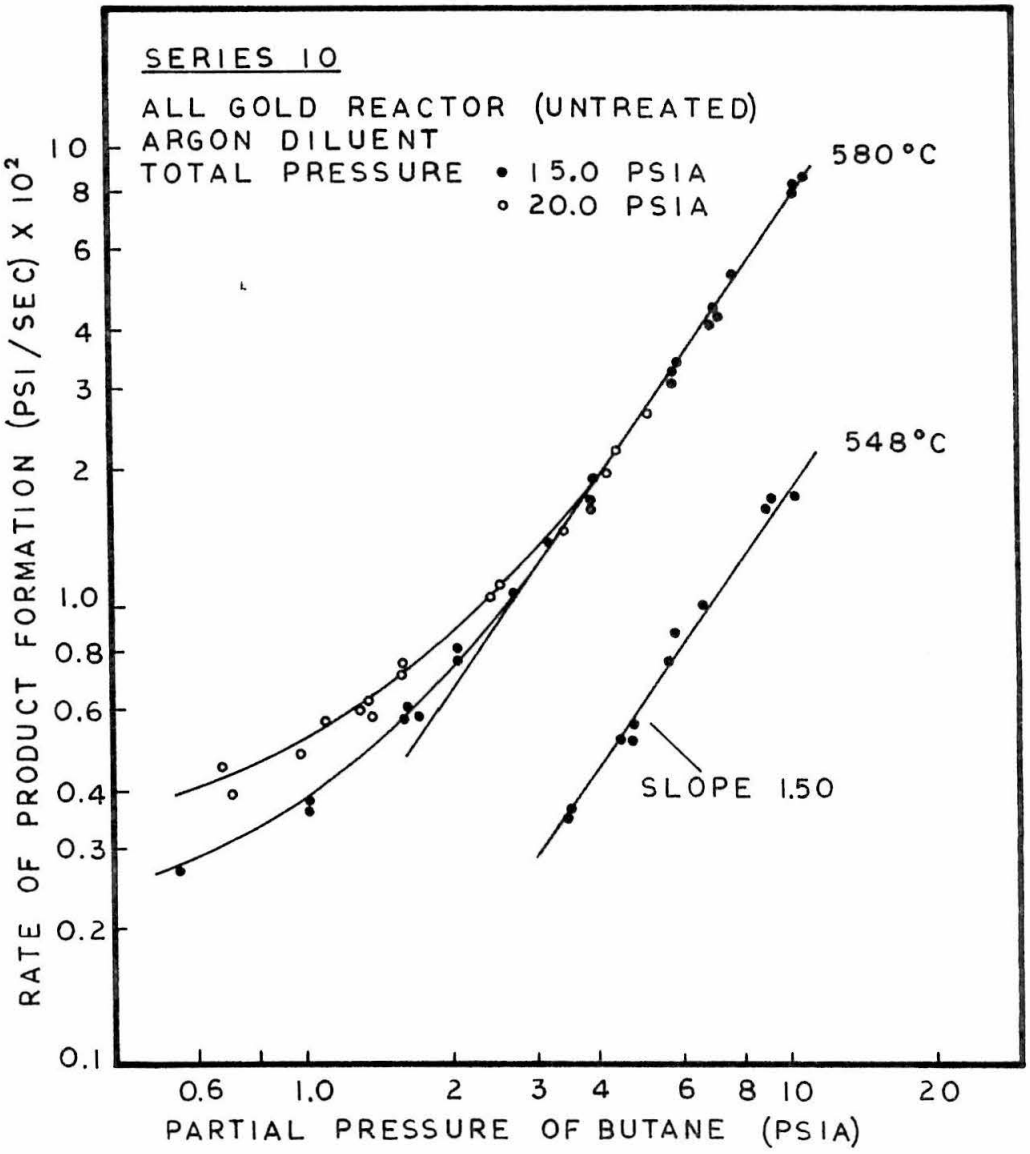


Figure 27. Rate of pyrolysis of n-butane as a function of temperature and pressure for the all-gold reactor (untreated).

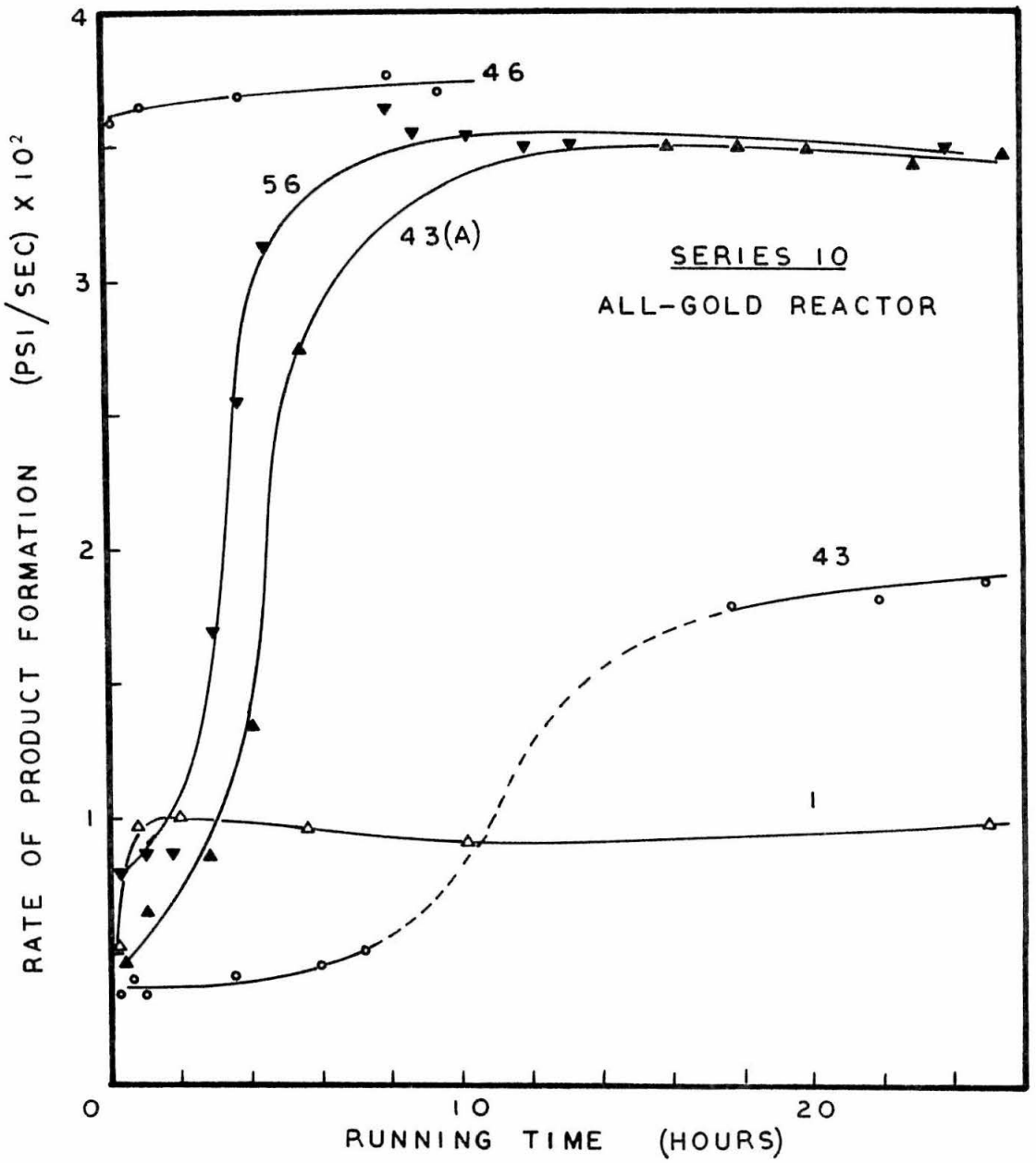


Figure 28. Variation in the rate of pyrolysis with running time for the all-gold reactor subjected to various chemical treatments.

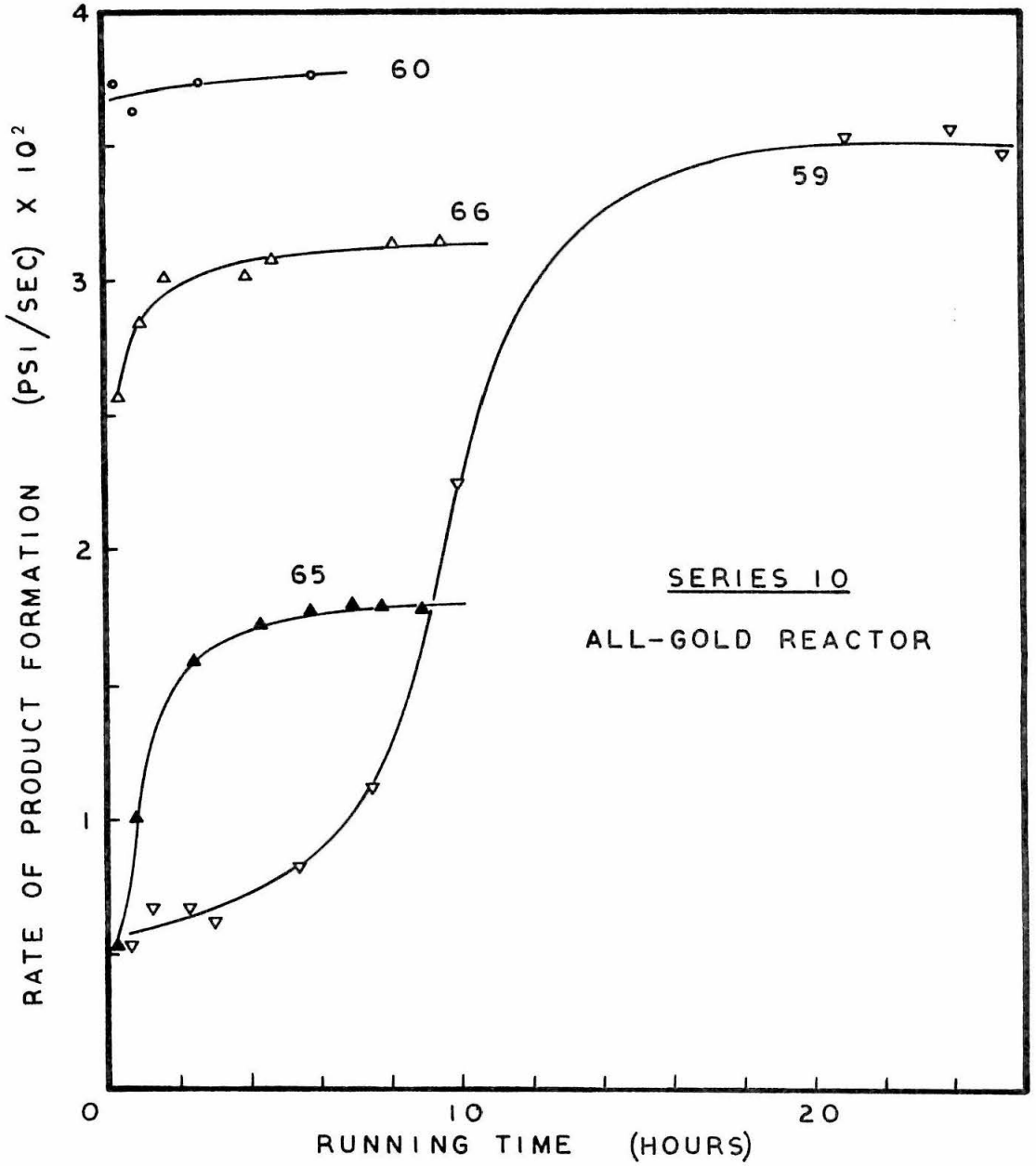


Figure 29. Variation in the rate of pyrolysis with running time for the all-gold reactor subjected to various chemical treatments.

Summary of Run Conditions, Figures 28 and 29 (Series 10).

Run 1. Was for the original, untreated reactor; p = 6.5 psia., T = 548°C.

Run 43. Was for reactor treated with oxygen for 12 hours followed by a 36 hour purge with argon; p = 5.85 psia., T = 568.5°C.

Run 43A. Was for reactor treated with oxygen for 8 hours followed by an acid-etch and argon purge; p = 5.50 psia., T = 566°C.

Run 46. Same reactor as for Run 43A, after an overnight pause; p = 5.40 psia., T = 567°C.

Run 56. Reactor after several further treatments with hot oxygen; p = 5.60 psia., T = 571.5°C.

Run 59. After a second acid etch treatment followed by an overnight purge with argon; p = 5.60 psia., T = 571.5°C.

Run 60. As for the previous Run but after an overnight pause in operation; p = 5.45 psia., T = 573°C.

Run 65. After a further 12 hour treatment with oxygen followed by degassing for 28 hours; p = 5.55 psia., T = 562°C.

Run 66. Was for the reactor subjected to its third acid-etch treatment followed by degassing for 24 hours; p = 5.50 psia., T = 564.5°C.

mental error, the asymptotic rates following the three acid treatments (Runs 43A, 59 and 66) were identical. The effect of the various acid treatments was not studied systematically; the exposure of gold surfaces to 30% nitric acid for periods of over 30 minutes should be entirely sufficient to remove traces of iron, copper or silver oxides.

Further tests were made to check on the effects of a high temperature degassing operation following the acid-etch treatment. Comparing the start-up curves for the various treatments it is evident that the high temperature degassing operation was very effective in reducing the time required to reach the asymptotic rate. Mattera et al (73) reported that the effect of treatment by nitic acid is solely to remove traces of impurity oxides from gold surfaces. Possibly the drift in the start-up period was due to traces of water adsorbed on the gold surface, though it would not be immediately obvious as to why adsorbed water should influence the pyrolysis. The electronic structure of gold permits a fairly easy promotion from the d to the s level. With activity in chemisorption generally confined to incomplete d orbitals it may be that some interaction between the adsorbed water and the gold could be reflected in the rate of pyrolysis.

Obviously much work remains to be done before the surface activity of gold can be considered understood. The results obtained using the microreactor were relatively in-

direct measurements of an assumed surface effect on a complex decomposition. Because of the many ways in which surface effects can arise in such a system, the evidence should be properly considered to be circumstantial until much more systematic studies using simpler reactions can be completed. The most fruitful experimental approach from this point would be to study the pyrolysis of n-butane in a batch reactor made of gold. The batch reactor would have the following advantages over the microreactor:

a. A batch reactor can be used over a wide range of surface-to-volume ratios.

b. All the surface in a batch reactor is exposed uniformly to the reactants.

c. The surface of a batch reactor can be easily inspected.

d. The batch reactor does not have a significant spread in residence times.

Bacause of the satisfactory reproducibility resulting from the acid-etch treatments the reactor was referred to as a "stabilised acid-treated reactor". The behavior of this reactor when used for systematic pyrolysis studies was the subject of the remainder of Series 10.

Series 10. Systematic Pyrolysis Runs Using an Acid-Treated, Stabilised Reactor.

A systematic set of runs was carried out using the acid-treated, stabilised reactor (Runs 70 et seq). Figure 30 summarises the rate-pressure data for this Series. Again, with the addition of argon to the system the order of the decomposition (with respect to the butane) decreased. The "break-off" effects for the all-gold reactor (Figures 27 and 30) were clearly more evident than the effect in the original reactor of Series 6 (Figure 6). One surprising feature of Figure 30 was the finding that the low temperature curve (529°C.) had a slope of 1.65; any order above 1.50 would certainly be incompatible with the accepted mechanism of pyrolysis. Assuming the effect is a genuine kinetic one, and is not due to some spurious complication in the low temperature runs, the only plausible explanation for the 1.65-order would be some heterogeneous contribution to the decomposition which becomes relatively more significant at lower temperatures.

Figure 31 is an Arrhenius plot of the temperature dependence of the rate of reaction at a fixed butane pressure. The data are correlated by the following expression:

$$k_p = A_p \exp(-E_p/RT) \qquad \text{psi.}^{-\frac{1}{2}}\ \text{sec.}^{-1}$$

where $A_p = 2.74 \times 10^{14}$ psi.$^{-\frac{1}{2}}$ sec.$^{-1}$ and $E_p = 65.2$ kcal./mole

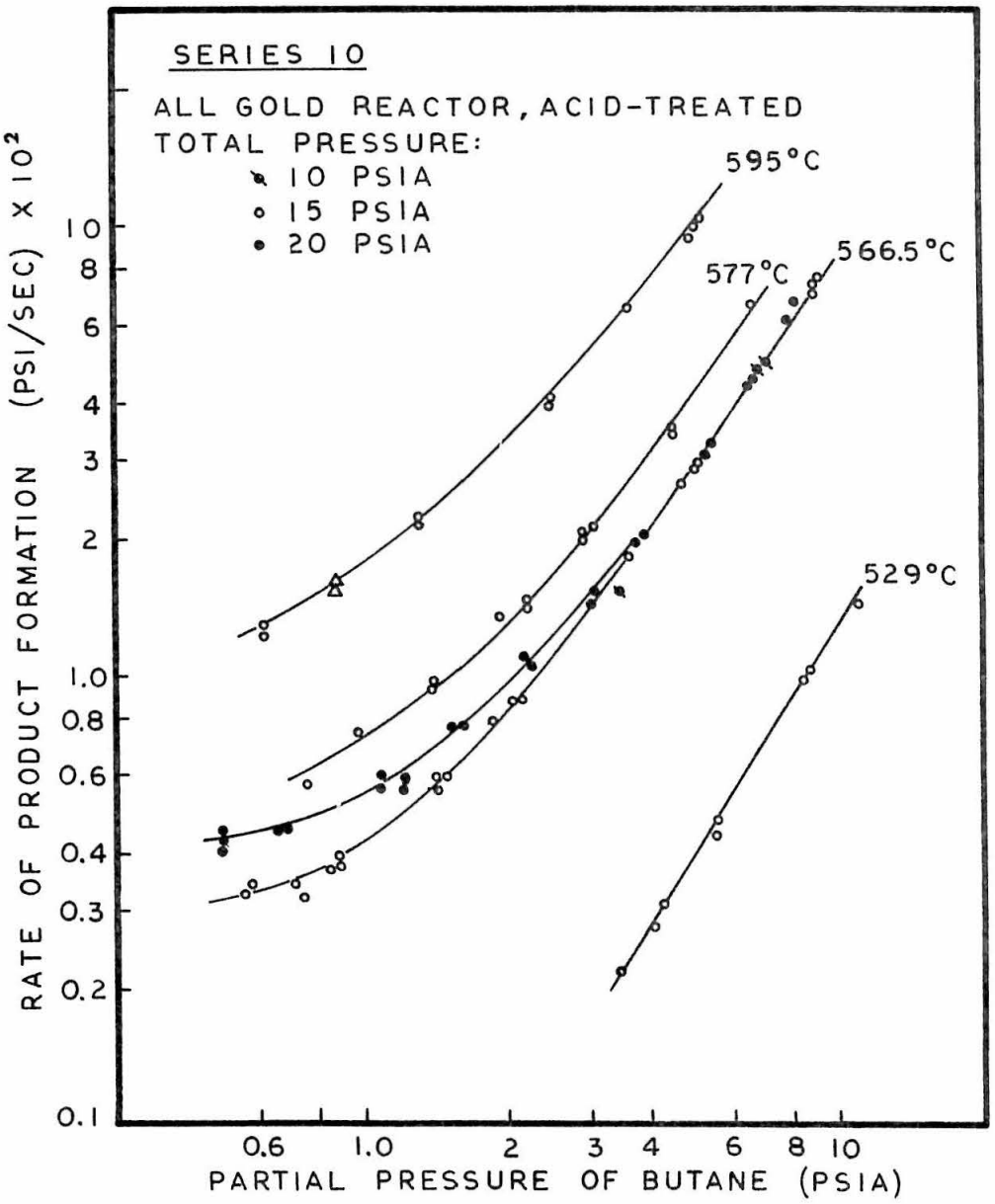


Figure 30. Pyrolysis of n-butane as a function of temperature and pressure, using the all-gold, acid-treated reactor.

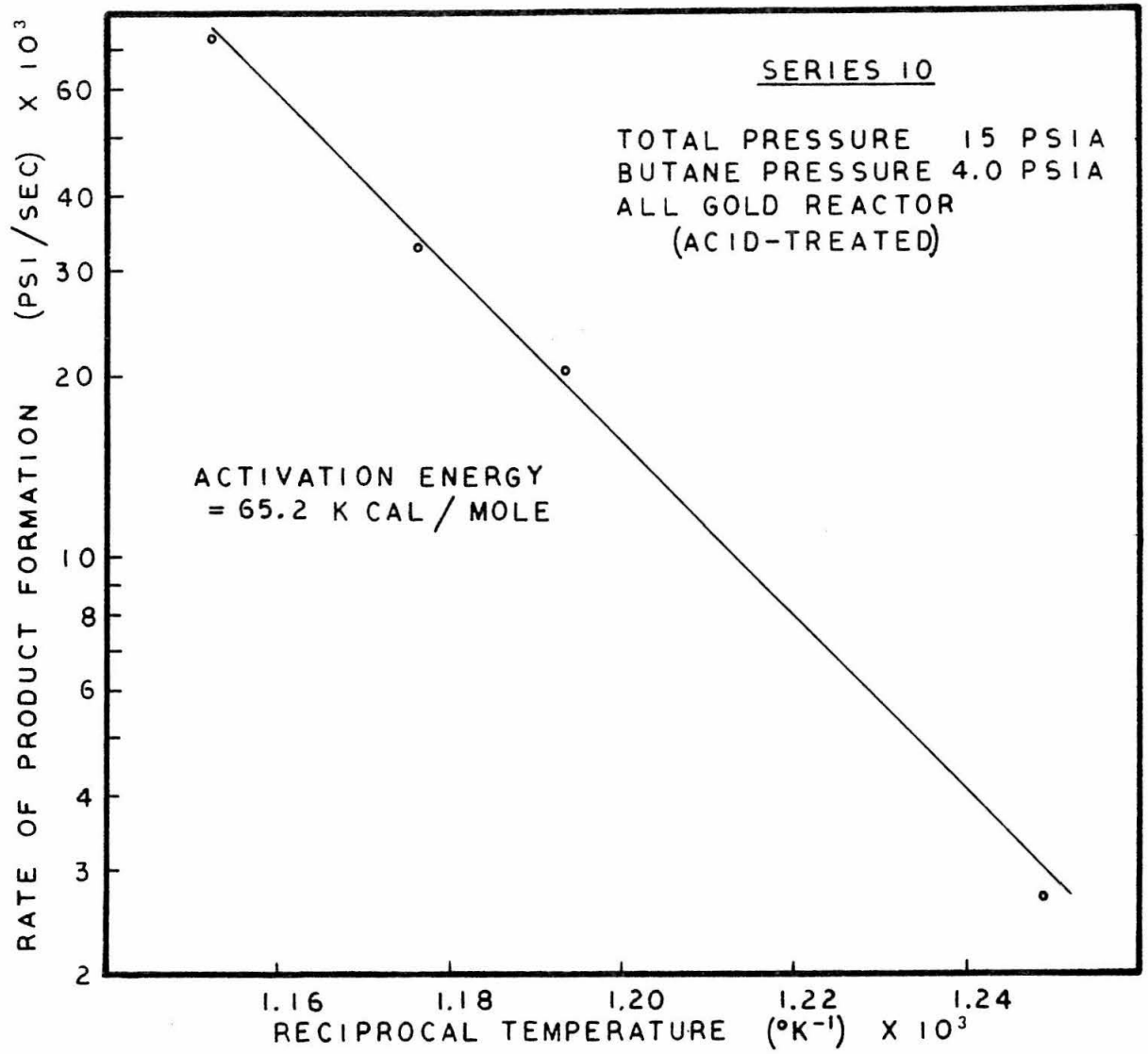


Figure 31. Arrhenius plot for the pyrolysis in the stabilised reactor.

This expression may be converted to the conventional expression (in concentration rather than pressure units) using the following standard relations for a reaction of order m:

$$k_c = k_p (RT)^{m-1}$$

where $k_c = A_c \exp(-E_c/RT)$

$$E_c = E_p + (m-1)RT \qquad A_c = A_p (RT)^{m-1} e^{m-1}$$

Evaluating the various terms at the mid-point of the temperature range (560°C.) the Arrhenius expression for the 3/2-order rate constant is:

$$k_c = 4.54 \times 10^{17} \exp(-66{,}000/RT) \quad \text{ml.}^{\frac{1}{2}}\ \text{mole}^{-\frac{1}{2}}\ \text{sec.}^{-1}$$

for the formation of cracked products.

Figure 32 is a plot of the variation of the ethylene-to-ethane ratio (α) as a function of the pressure and temperature. The maxima in these curves are unexpected in that the normal mechanism of pyrolysis (with no diluent present) predicts a continuous increase in α with decreasing partial pressure of the butane. Runs conducted at a high dilution of the butane (viz. Runs 87 to 92a) showed a slight increase in the propylene-to-methane ratio. These findings were to be checked further in Series 13. Any scheme proposed to account for the "break-off" phenomenon

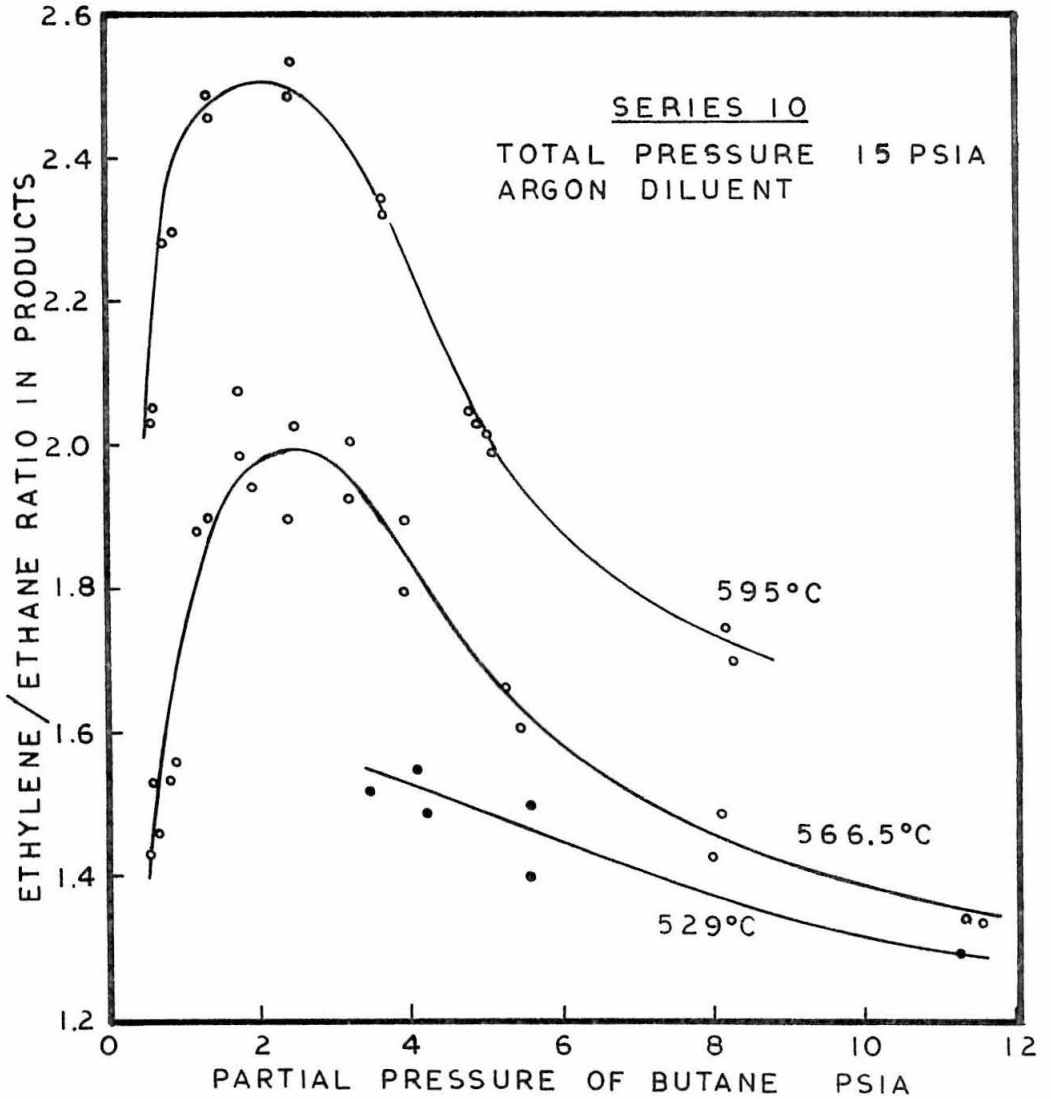


Figure 32. Variation in the ethylene-to-ethane ratio with temperature and pressure.

should be able to account for these drifts in the product composition at high dilutions of n-butane.

A comparison of overall rate data from several sources.

The most recent studies on the pyrolysis of n-butane are due to Purnell and Quinn (19), Sagert and Laidler (22) and Wang, Rinker and Corcoran (10). Data from these sources will be compared with data from Series 10.

The following analytical expressions were given:

(S-L): rate constant for the disappearance of butane:

$$k = 3.24 \times 10^{15} \exp(-59{,}900/RT) \quad \text{ml.}^{\frac{1}{2}}\ \text{mole}^{-\frac{1}{2}}\ \text{sec.}^{-1}$$

(P-Q): rate constant for the rate of formation of ethane:

$$k = 3.80 \times 10^{14} \exp(-58{,}300/RT) \quad \text{ml.}^{\frac{1}{2}}\ \text{mole}^{-\frac{1}{2}}\ \text{sec.}^{-1}$$

At 530°C. and assuming the ethane to be 9.5% of total products, the rates of decomposition calculated from the above expressions differ by a factor of 1.8. Evidently the results obtained using quartz (22) and pyrex (19) reactors were only in fair agreement.

The data reported by Wang et al (10) were faster than those reported by these other workers. For example, at 550 °C. Wang reported a first-order rate constant of 11×10^{-3} sec.^{-1} (at 1 atm. pressure) giving a rate at 760 mm. pressure of 8.4 mm./sec.. (In Figure 6 of the paper by Wang et al the rate constants were erroneously over-estimated by a factor of 10). Data of Sagert and Laidler at 550°C. gave a 3/2-order rate constant of 5.65×10^{-5} sec.^{-1} $\text{mm.}^{-\frac{1}{2}}$

which would predict a rate at 760 mm. pressure of 1.24 mm./sec.. It is not immediately obvious why the rate data of Wang were so high; possibly there were surface effects in the inlet and outlet sections of his reactor.

The accompanying Arrhenius plot (Figure 33) summarises the 3/2-order decomposition constants. The S-L curve was taken from Figure 4 of the original paper. The P-Q curve was taken from Figure 7 of the original paper (19); it was assumed in this evaluation that the rate of decomposition of the butane was half of the total rate of product formation. For the purposes of comparison, Wang's data were re-evaluated from their original first-order rate constants and corrected to the equivalent 3/2-order constants. Turning to the data taken in Series 10, the evaluated rate constants for the four temperatures used in this study are included in Figure 33.

Figure 33 clearly indicates that the pyrolysis data taken on the gold reactor were intermediate between the data taken on the quartz (S-L) and the pyrex (P-Q) reactors. Overall, the rates determined by Wang et al and by Sagert and Laidler differed by a factor of about 5. The activation energy for the reaction in the gold reactor (66 kcal./mole) was significantly higher than that determined in the quartz and pyrex reactors (about 59 kcal. per mole). However the results of Series 6 (and subsequent

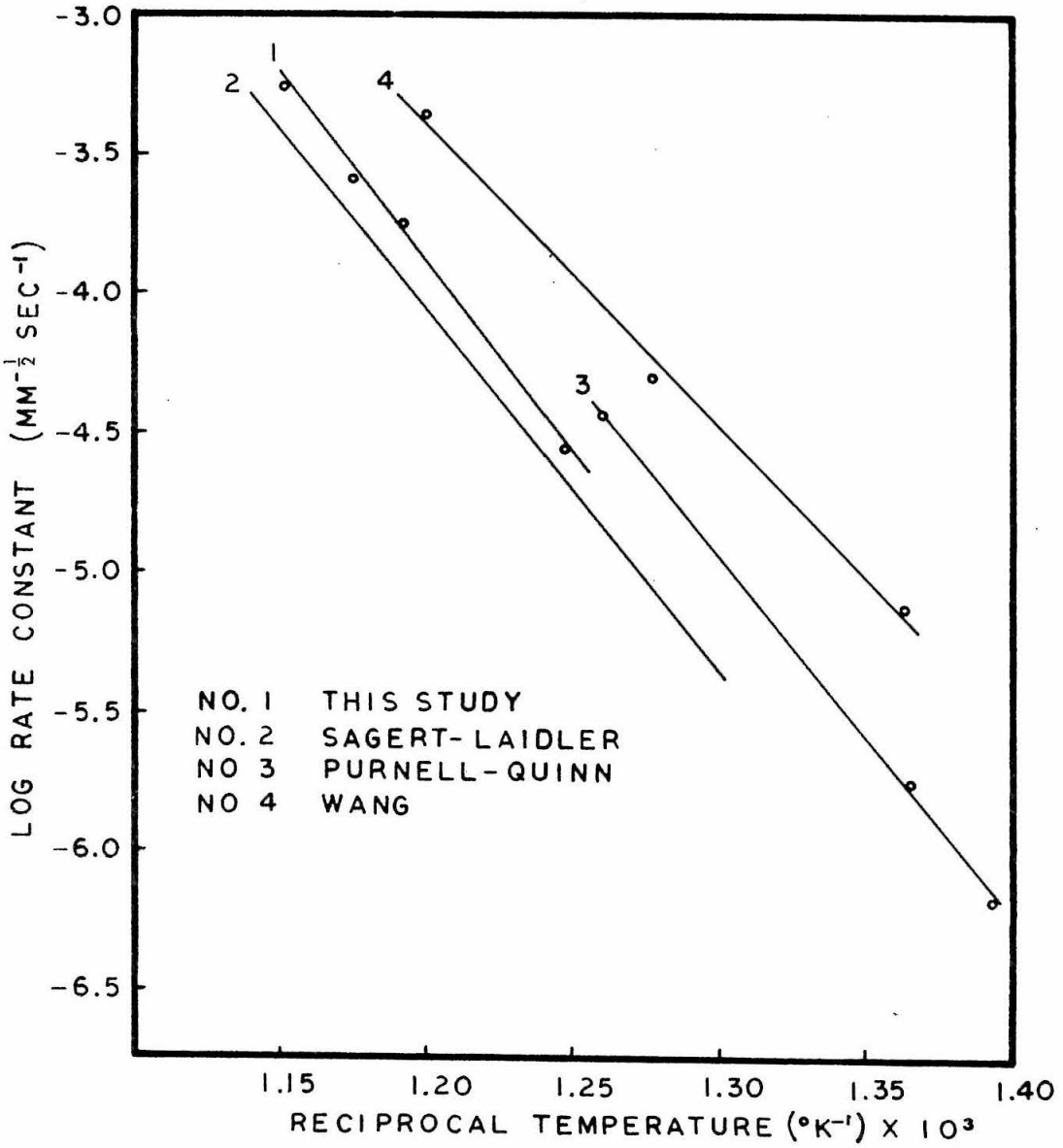


Figure 33. Summary Arrhenius plot of the decomposition constants reported by several workers.

series) showed that the product distributions were very closely comparable in reactors of both gold and pyrex. It is safe to conclude therefore that the difference between the activation energies was mainly due to the temperature gradients in the gold system, and the resulting errors in the mean temperature of the reactor. The possibility of a fortuitous cancelling of errors should not be entirely discounted. In order to satisfactorily demonstrate the homogeneity of the decomposition in a gold reactor it would be necessary to perform experiments under conditions of lower surface-to-volume ratio.

SERIES 7.

On the temperature gradients in the reactor.

In the calculations of the rate constants for the pyrolysis, the reactor has been assumed to be isothermal. Series 11 was conducted to find out the effects of the temperature gradients which were imposed on the reactor by the observed gradients in the thermostat. The additional problem of the temperature gradient due to the heat of reaction will be discussed in an Appendix to this Thesis.

Experimental evidence taken in the first few runs of Series 11 related a measurement of the overall rate of pyrolysis to the temperature profile in the thermostat. Two qualifications should be conceded regarding these profiles.

Firstly, the thermocouple did not accurately represent the air temperature in the thermostat; this error was due to heat conduction along the sheath of the thermocouple. Secondly, the temperature profile was measured in the air space next to the reactor tube; the profile in the air space would be an unreliable indication of the profile in the reactor tube. The temperature gradient in the air space was upto 25°C. over the length of the reactor. Although the high thermal conductivity of the gold would serve to eliminate the more severe gradients, by the same token there would be a significant heat loss from the ends of the reactor tube. The problem defied a theoretical analysis because of the complexity of a realistic model for the heat-transfer processes within the thermostat. No data were taken of the actual gradient in the reactor tube.

The empirical approach which was used in Series 11 was to compare the effects of different heater settings (which altered the gradients in the air space) on the overall rate of pyrolysis. In two runs, (Nos. 18a and 19), the temperature of the reactor support block was changed by 25°C.. With data corrected to the same mean reactor temperature, the rate changed by only 25%. Ordinarily, a change of 25°C. in the reactor temperature would have changed the rate of pyrolysis by a factor of about 3.0. These figures were tentatively taken to show that temperature gradients in

the thermostat did not seriously affect the overall rate of pyrolysis. For most subsequent runs the thermocouple was set at a point 1.5 inches below the lid of the thermostat. The temperature recorded by this thermocouple was taken as the mean reactor temperature.

Several recommendations can be made in the light of the above comments:

1. The reactor support block was undoubtedly responsible for a major contribution to the temperature gradient in the thermostat. This block should be modified or eliminated. Further attempts should be made to operate a thermostat on the recirculating-air principle.

2. To ensure that the thermocouple measures the air temperature accurately it may be possible to cut back the sheath away from the thermocouple junction. This would reduce heat losses from the junction.

3. Because the errors involved are mostly due to temperature gradients in the upper end of the thermostat, they would become relatively less important with increasing length of the reactor. It would not be desirable to use a reactor less than one foot in length with the temperature gradients as they existed in the thermostat.

4. The uncertainty surrounding the mean temperature of the reactor throws the estimates of the activation energies into doubt. Because of this uncertainty the remaining series

concentrated on further aspects of the pyrolysis at a fixed temperature. The value of the overall activation energy estimated in Series 10 would be identical with that given by Purnell and Quinn if there were a cumulative error of 5°C. throughout the temperature range of the study.

Pyrolysis of n-butane with a nitrogen diluent.

A detailed set of pyrolysis runs were carried out using a nitrogen diluent. The rate-pressure characteristics (Figure 34) were similar to those observed in earlier series which used an argon diluent. The data from both Series 10 and 11 showed that, at the higher total pressures, (15 and 20 psia.), the rate of pyrolysis tended towards an asymptote at low partial pressures of n-butane. In the final Series (No. 13) an attempt was made to determine whether or not an asymptote was established.

On one occasion, at the end of Series 11, it was found that after an overnight shutdown the rate of pyrolysis fell by a factor of about two and that the product analysis showed an excess of propylene. After a short treatment with oxygen followed by degassing the rate of pyrolysis went back up to its original value. The cause of this shift in the rate is not immediately clear; possibly the effect may be ascribed to carbonaceous deposits which could consolidate during the shutdown interval. Purnell and Quinn (18) noted an inhibition effect when carbonaceous deposits were formed

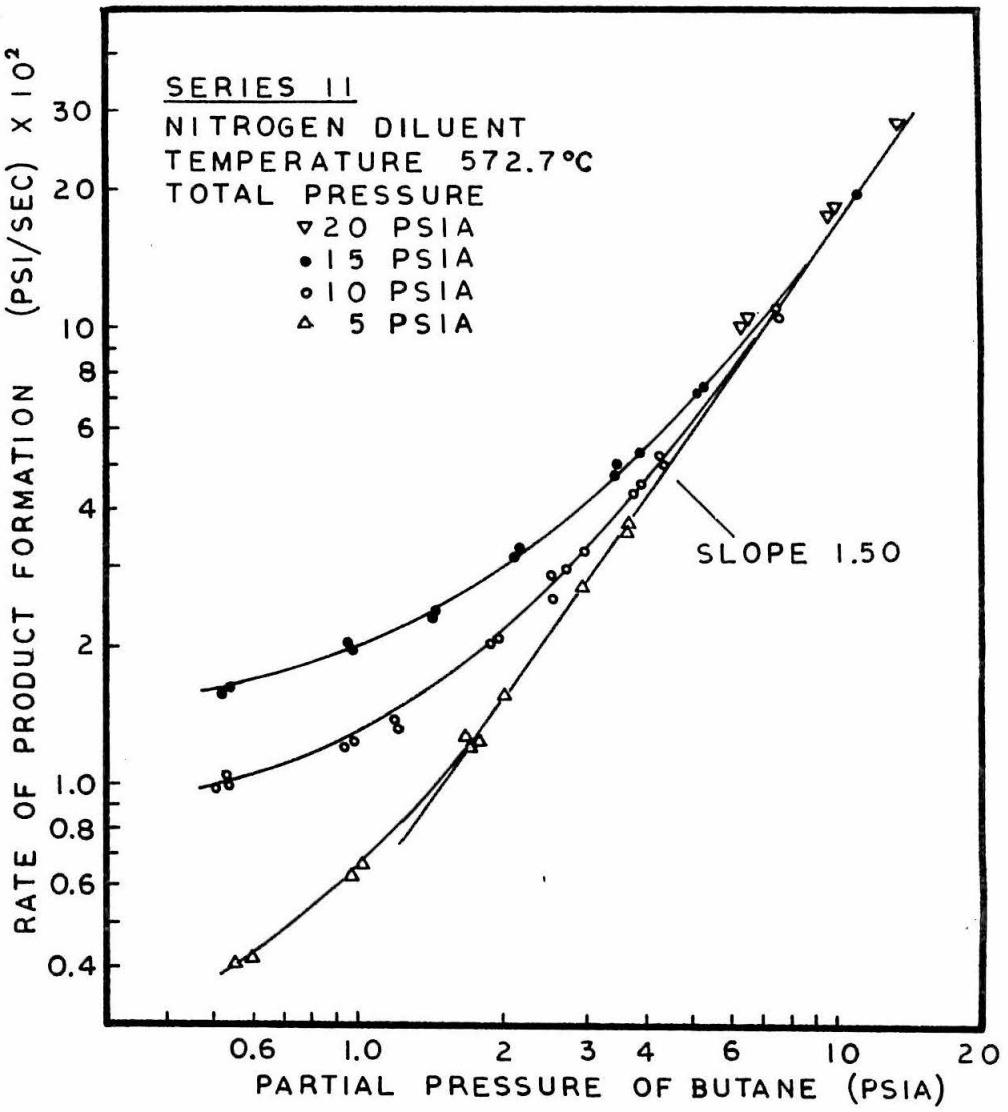


Figure 34. The pyrolysis of n-butane at several pressures, using a nitrogen diluent.

in a pyrex reactor. There is insufficient evidence to show whether or not the carbonaceous deposits are the same in reactors made of different materials of construction.

SERIES 12.

Pyrolysis using several diluent gases.

It was interesting to determine whether or not the "break-off" phenomenon was dependent on the nature of the diluent gas. In Series 12 a number of diluent gases were employed, viz. argon, helium, nitrogen and carbon dioxide. The rate-pressure curves (Figure 35) show that, within the limits of experimental error, the behavior of the pyrolysis in the "break-off" region was independent of the type of diluent gas. The experimental errors were mainly due to errors in the calibration of the diluent flowmeter. This was a surprising result considering the fact that the "break-off" effect was clearly dependent on the presence of an inert gas. The implications of this finding will be considered in a treatment of the "break-off" effect.

SERIES 13.

The effects of various contaminants on the pyrolysis.

In this final Series of runs the effects of various contaminants were studied. Ethylene, propylene and hydrogen are products of the decomposition of n-butane and may be

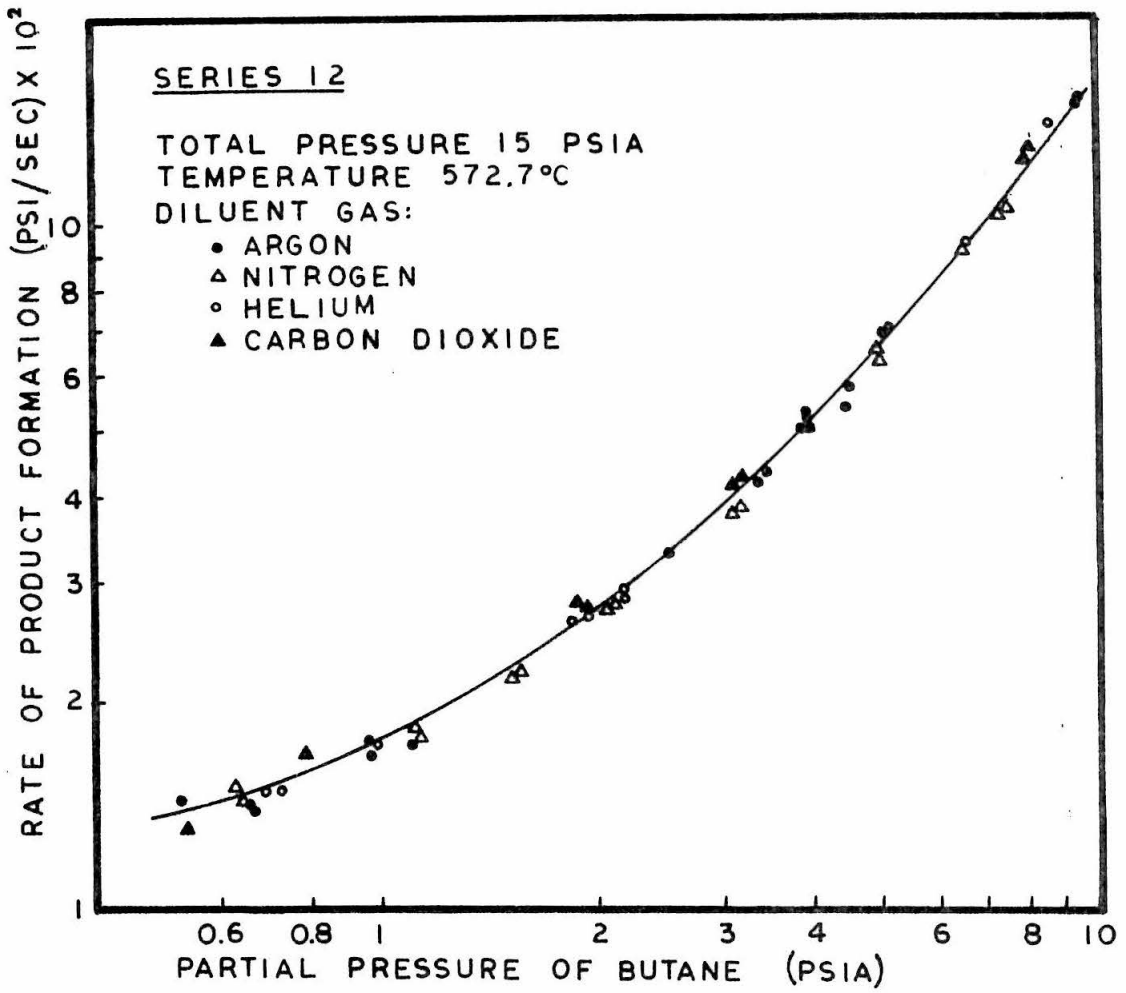


Figure 35. Rate-pressure curves for the pyrolysis of n-butane in several diluent gases.

capable of influencing the pyrolysis of butane in its later stages; these components were added (separately) as contaminants in the n-butane stream. A few runs were performed with oxygen as a contaminant; these runs were performed at the relatively high temperature of 573°C. so that the reaction could not strictly be classified as a partial oxidation process.

Propylene.

Propylene is well known to be an inhibitor though the mechanism of inhibition is not well understood (30,60). One of the early theories of the inhibition effect was that the propylene was capable of abstracting "active" free radicals and replacing them by less active radicals. However, under the normal conditions of pyrolysis the rate of combination of a methyl radical with propylene to give a butyl radical would be much less than the rate of decomposition of the butyl radical. A simple combination mechanism could not account for the large inhibition effects which have been recorded. Further evidence against the oversimplification of inhibition mechanisms is that cited by Kallend and Purnell; they found at least 20 products resulting from the reaction of methyl radicals with propylene at temperatures above 350°C. (70).

Quinn (60) presented evidence to show that the propylene is reactive under the conditions of the pyrolysis

of n-butane. He suggested that the decomposition of a propylene - butane mixture should be regarded as a co-pyrolysis involving two mutually interacting chains. The addition of propylene resulted in greatly increased yields of butenes though the proportions of cracked products were only slightly affected.

Data taken in earlier series (Nos. 6 and 7) as well as the first few runs of Series 13 showed that the rate of pyrolysis fell-off rapidly with increasing conversion (Figures 8 and 36). The fall-off has usually been assumed to be due entirely to the presence of propylene as a major product of the pyrolysis.

Results of a set of runs in which propylene was added to the feed butane are given in Figure 36. In preparing this plot it was assumed that the yield of propylene due to the reaction was identical with the yield of methane. By utilizing the data of Figure 36, an integrated solution for the yield - time curve could be built up. In Figure 37 the integrated solution is compared with the experimental yield-time curve. Evidently, inhibition by propylene accounted for a major part of the inhibition effect. The integration was performed in a step-wise ascending fashion using time intervals of 0.5 seconds. Use of a smaller increment would bring the calculated conversion curve nearer to the experimental curve. In calculating the integrated solution no

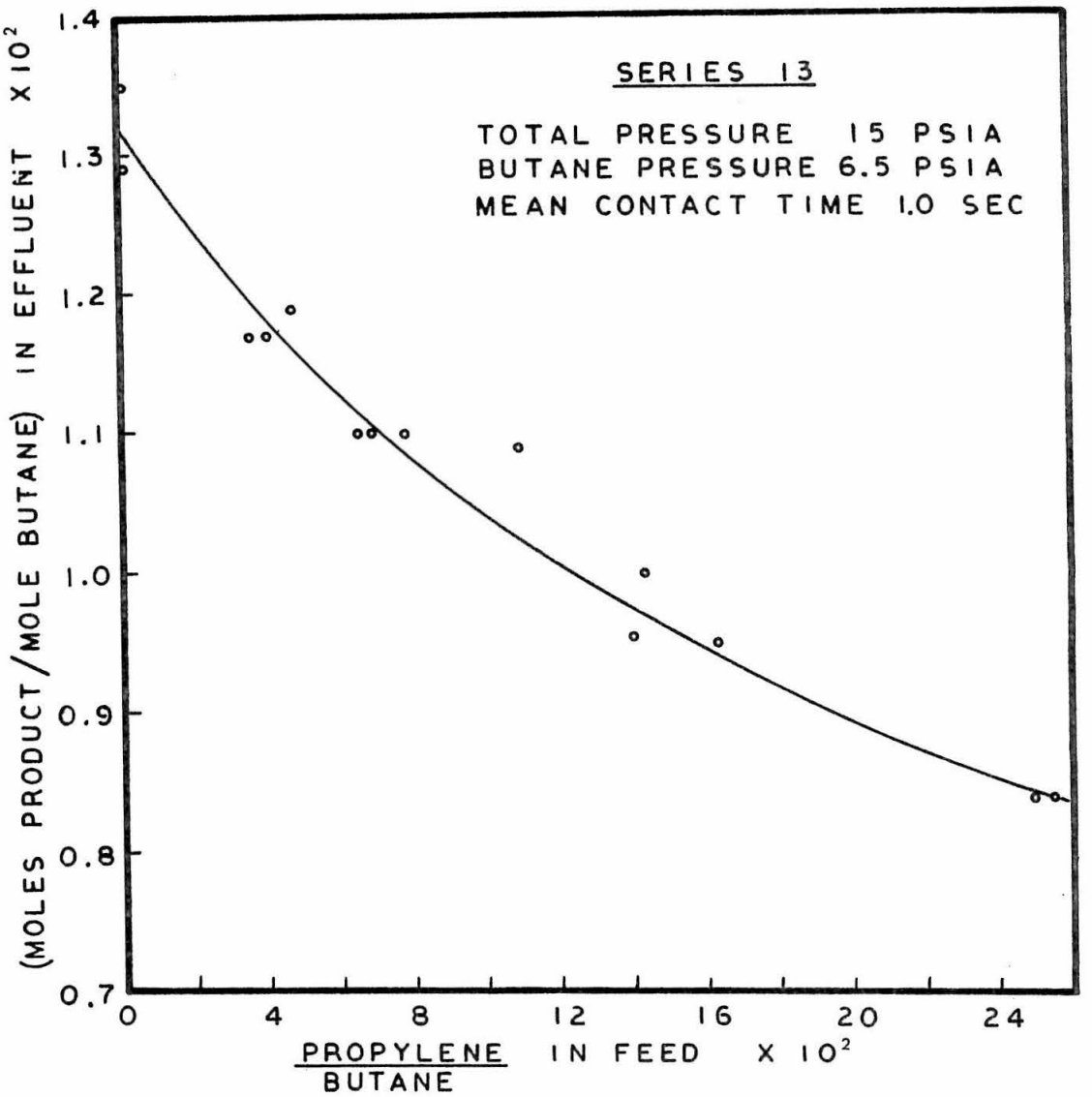


Figure 36. The inhibitory effect of propylene on the pyrolysis of n-butane.

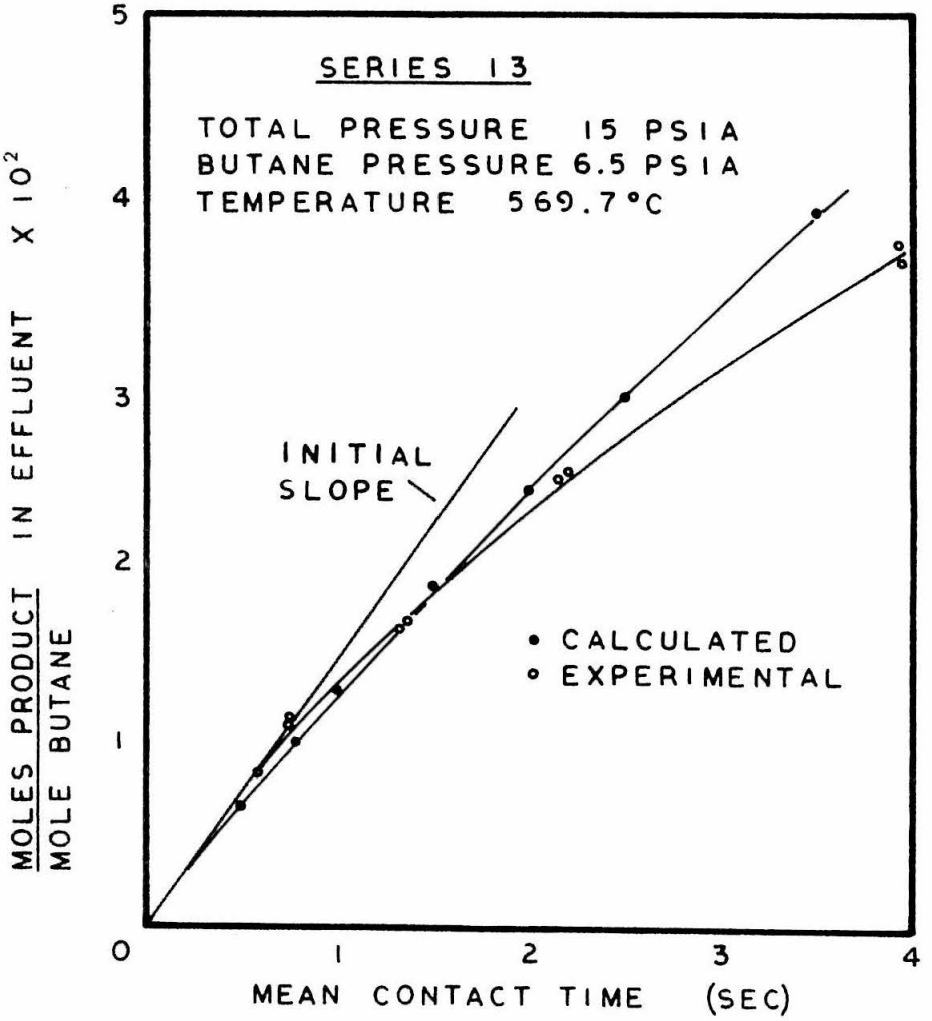


Figure 37. Calculated and experimental yield-time curves for the pyrolysis.

allowance was made for the consumption of propylene. On comparing Figures 36 and 37 it is evident that with increasing contact time the inhibition effect was more marked whereas with increasing concentrations of propylene the inhibition effect was less marked. Thus the fall-off in the rate of pyrolysis was more related to the increased contact time than to the increased concentration of propylene. This finding constitutes indirect evidence for a branching-chain inhibition effect. Unfortunately, the formation of butenes in the co-pyrolysis was not checked; a comparison with the results of Quinn (60) would be most interesting in checking the possibility that the inhibition effect is surface dependent.

Hydrogen.

Benson (23) noted that some pyrolytic decompositions are catalysed by hydrogen. A single Run was made (No. 14) in which the diluent contained a high level of hydrogen (11.5%). The data revealed that the hydrogen exerted no significant catalytic effect under the conditions set for the Run. In fact there was a slight inhibitory effect; this effect may have been due to errors in the flow-metering of the argon - hydrogen diluent.

Ethylene.

An attempt was made to determine whether or not

ethylene could play any role in the inhibition of the pyrolysis of n-butane. Three sets of runs were performed (Nos. 46 to 48b) with various concentrations of ethylene in the butane feed. Within the experimental limits of error the addition of ethylene had no effect on the rate of pyrolysis or on the distribution of the cracked products. If corrections were to be applied to account for the dilution effect of the ethylene and for the effect of the ethylene on the flowmeter calibrations, the data would have shown even closer agreement. Purnell and Quinn (54) have suggested that in the presence of ethylene the butyl radical is capable of undergoing isomerisation. On that basis one would have expected some change in the product composition with the addition of ethylene.

Of the major products of pyrolysis (hydrogen, methane, ethane, ethylene and propylene) only propylene can be shown to significantly affect the pyrolysis. Methane and ethane are expected to be stable products of the pyrolysis below 600°C.. Butenes are minor products of the pyrolysis (less than 1% of the total products). The influence of butenes on the pyrolysis was not checked. Indirect evidence obtained using research-grade butane (butene-free) and instrument-grade butane (containing about 1000 ppm. total butenes) showed that the influence of trace levels of butenes on the pyrolysis was negligible. The inhibition of the normal

pyrolysis can therefore be ascribed solely to propylene.

Oxygen.

A number of runs (Nos. 15 to 28a) were performed in which oxygen levels in the diluent gas were varied over a wide range. These runs were not intended as partial oxidation experiments but rather were to show the effects of oxygen on the pyrolysis. At 572°C. the oxygen was removed extremely rapidly; for example, with 11.5% oxygen in the diluent the oxygen was completely removed at contact times in excess of 1.5 seconds. In most of the runs the behavior of the system was essentially that of a rapid oxidation followed by a normal pyrolysis; this was of course especially true for runs with low levels of oxygen. In the runs with a high concentration of oxygen in the diluent (11.5% oxygen) the product yield-time curves (Figure 38) were similar to those reported for Series 8, which used an untreated reactor. Surprisingly enough, the conversions attained in the untreated and the acid-treated reactors were closely comparable.

Data in the accompanying table summarise the effects of different levels of contamination by oxygen. It is quite evident that the presence of oxygen has a drastic accelerating effect on the rate of formation of butenes but has a mildly inhibiting effect on the formation of the cracked products. 1,3-Butadiene was formed in detectable amounts

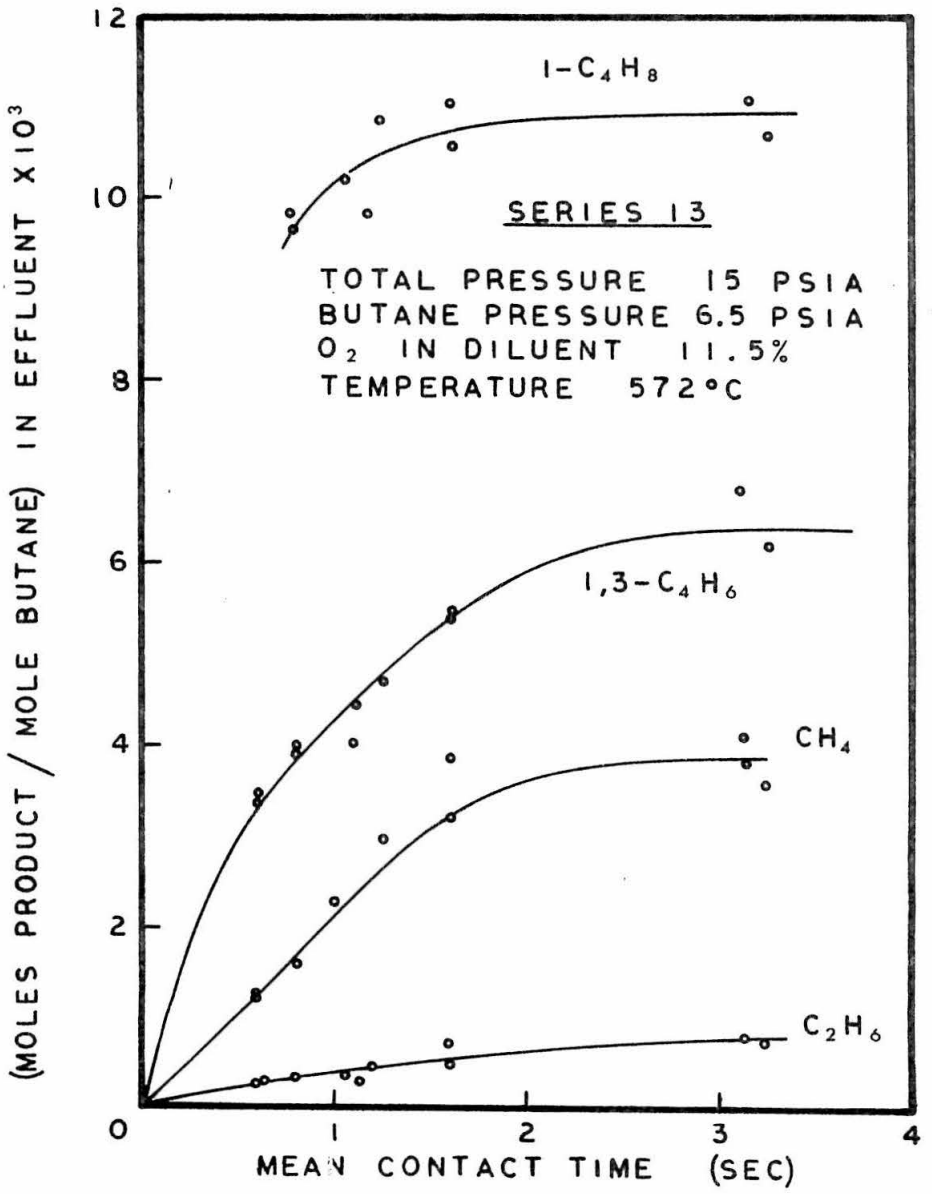


Figure 38. Yield-contact time curves for the partial oxidation in an acid-treated reactor.

only when oxygen was present. The mechanism of the inhibition effect is not entirely known. Benson (65) reported that even at low temperatures (100°C.) oxygen would react rapidly with all alkyl radicals ($R^{\cdot}$) to form alkoxy radicals ($RO_2^{\cdot}$) and thus interfere with the formation of cracked products. A similar view was presented by Niclause et al (36). The data of Series 13 clearly show that the formation of both methane and propylene was moderately inhibited by oxygen, the formation of ethane was strongly inhibited, and the formation of ethylene was not markedly affected by the presence of oxygen.

The yield of carbon monoxide in the partial oxidation reaction was again very low, or undetectable, in most of the runs. It is known that the chemisorption of carbon monoxide onto gold is rapid (50). In several instances adsorbed carbon monoxide is only desorbed as carbon dioxide under oxidative conditions (50); it is not known whether or not this mechanism of carbon dioxide formation could apply to the partial oxidation in a gold reactor.

Pyrolysis at low pressures of n-butane.

Earlier experiments (Series 11) had indicated that the rate-pressure curves tended towards asymptotes at high dilutions of the n-butane. To find out whether or not an asymptote was established an extended series of runs was

A comparison of data to show the effects of oxygen.

	Run Number.			
	17	22a	27c	28a
Oxygen level in diluent.	11.5%	2.95%	200 ppm.	0-5 ppm.
Temperature (°C.)	571.5	572.2	570.0	572.2
Butane pressure (psia.)	6.76	6.30	6.25	6.35
Contact time (sec.)	1.04	1.15	1.16	1.09
Conversions as (moles product/moles butane) in effluent x 10^2				
Methane	0.23	0.25	0.47	0.44
Ethane	0.04	0.06	0.15	0.16
Ethylene	0.26	0.20	0.27	0.26
Propylene	0.22	0.23	0.45	0.44
1-Butene	1.06	0.91	0.06	0.006
t-2-Butene	0.64	0.50	0.025	0.006
c-2-Butene	0.39	0.32	0.017	0.002
1,3-Butadiene	0.47	0.50	neg.	neg.

undertaken at high dilutions of the butane. The runs were performed at a total pressure of 20 psia. which was the maximum pressure at which the apparatus could be reliably operated. An automated cathetometer capable of reading to $\pm$ 0.005 cm. was used to record the differential head on the butane flowmeter. The lowest partial pressure of butane which could be reliably studied reflected the problems of metering the low flowrates of the butane and also of the chromatographic analysis of the highly diluted products of the reaction. The data (Figure 39) showed no remarkable variation with decreasing pressures of butane; under the conditions of this set of runs an asymptote was not reached. The partial pressure of butane ranged over an order of magnitude below the "break-off" point. Two runs were performed to demonstrate the fact that the rate of reaction was not dependent on the flowrate through the reactor. Again a maximum in the α - p curve was found and the propylene-to-methane ratio tended to increase at lower partial pressures of the butane (Figure 40).

On the formation of butenes in the pyrolysis.

A summary of the data for the formation of the butenes in the pyrolysis is included in the appendix section (No. 1). These data were all taken at 572°C. on the acid-treated reactor but otherwise under a range of contact times and pressures. The results, surprisingly enough, indicated

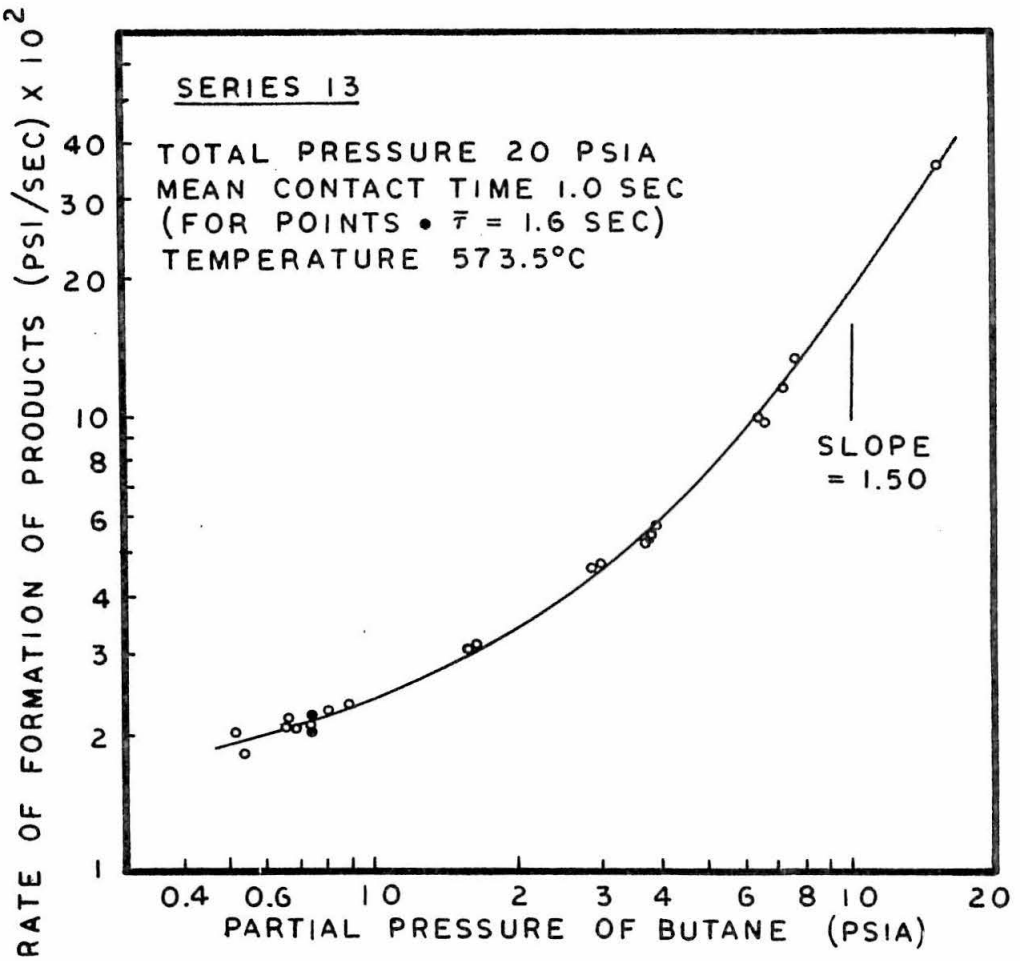


Figure 39. Rate-pressure curve for the pyrolysis at high dilutions.

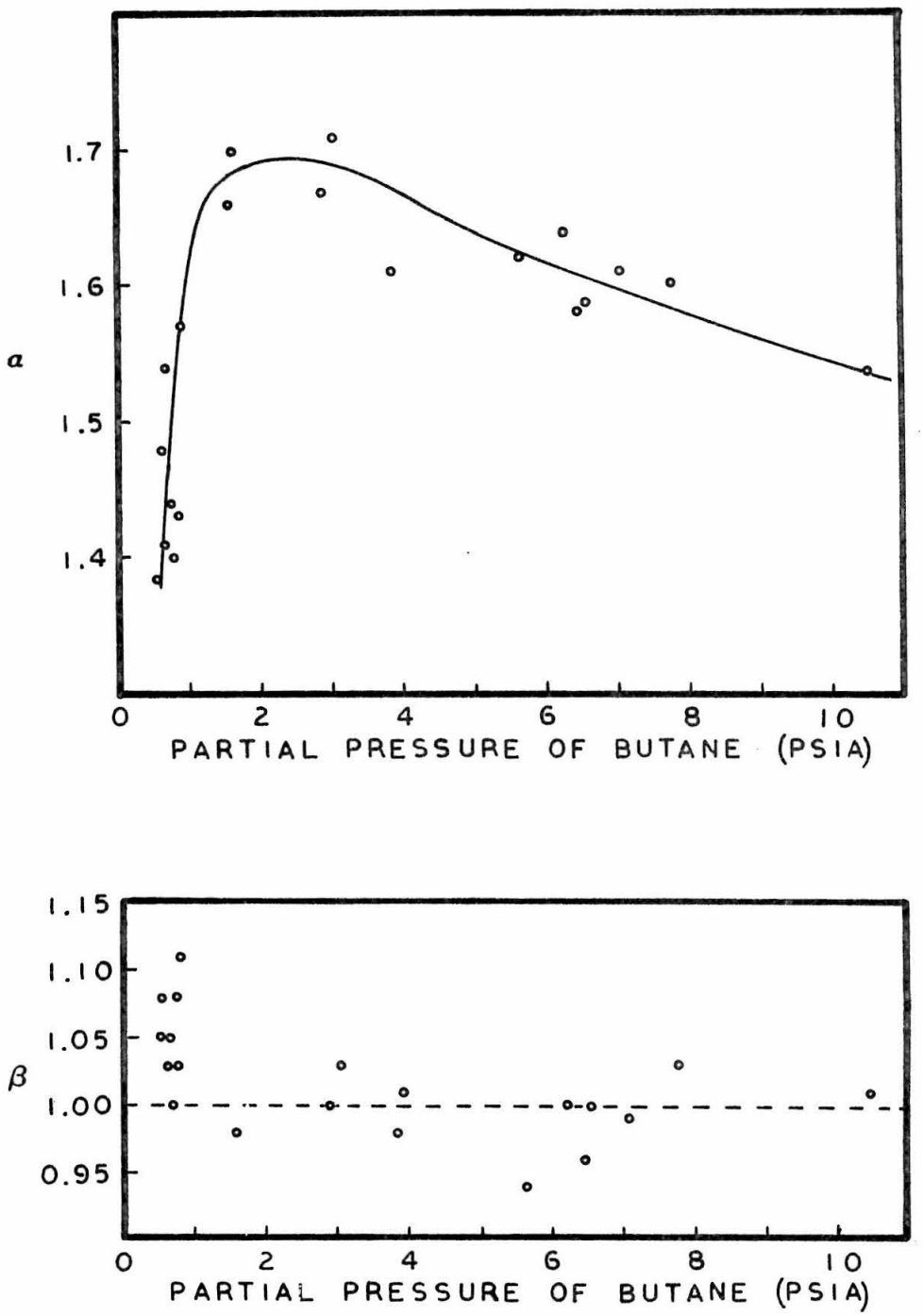


Figure 40. The variation of α and β with the partial pressure of n-butane.

that the total butenes formed were about 1% of the total products, under all conditions. Even in Series 13 where the contact time was varied between 0.58 and 4.04 sec. (Runs 1 to 5) the proportion of butenes only varied from 0.79 to 1.1% of the total cracked products. No other higher products were ever found in the pyrolysis of n-butane in the gold reactor. It would have been possible to detect any component whose concentration exceeded 5% of the total concentration of the butenes, provided its retention time was not excessive. The 1,3-butadiene, 1-pentene and cyclopentene found by Purnell and Quinn (19) were not observed in pyrolysis runs with the gold reactor.

The figures given above are comparable with those given by Purnell and Quinn (maximum proportion of 1% at 530°C.) and those given by Sagert and Laidler (1.4% at 570°C., 202 mm. and 15% decomposition); those workers reported about a quarter of the total butenes as 1,3-butadiene. By contrast, in the gold reactor the formation of 1,3-butadiene was only associated with the presence of oxygen in the system (p.123). Purnell and Quinn had no comments on the mechanism of butene formation. Sagert and Laidler suggested that a unimolecular decomposition of the butyl radical (to give $H^{\cdot}$ and C_4H_8) could only account for a small fraction of the observed yields of the butenes. They suggested that the remainder of the butenes was due to a surface dehydrogenation or a small molecular component of

the reaction. They also noted that it was difficult to explain the formation of 1,3-butadiene by any chain mechanism.

The various possible sources of butenes in the products of pyrolysis are as follows:

1. Butenes would be formed from the decomposition of iso-butane which was a trace component in the feed butane. A typical sample of n-butane (Research grade) would contain about 0.005% iso-butane. Assuming the two butanes decompose at comparable rates the proportion of butenes to cracked products would be about 0.005%. In fact it is known (9) that the iso-butane decomposes at a slower rate than n-butane.

2. The data of Series 13 clearly show the formation of butenes to be enhanced by the presence of oxygen. The pyrolysis studies were performed in the absence of oxygen (i.e. less than 2 ppm.). This precaution was not so rigorously enforced by other workers.

3. There is a possible surface effect, as suggested by Sagert and Laidler (22). It would be difficult to explain the close agreement between the results of the various workers solely on the grounds of a surface effect because of the wide variations in the type of surface and in the surface-to-volume ratio which have been used.

4. Quinn (60) presented data to show that the addition of propylene to the n-butane resulted in increased yields

of butenes. His finding affords some justification for the claim that the butenes are secondary products in the pyrolysis of n-butane. Secondary reactions alone would not account for the yield - time characteristics of butene formation because the proportion of butenes in the products does not tend (smoothly) to zero with decreasing contact time.

No one of the above factors can be clearly shown to predominate in the formation of butenes. The elucidation of the mechanism of formation of butenes remains to be completed and will require some refinements in the chromatographic analysis.

On the formation of hydrogen in the pyrolysis.

Assuming the mechanism for the pyrolysis proposed by Purnell and Quinn, (19), a mass-balance on the hydrogen would give the yield of hydrogen as being half the differential yield of ethylene and ethane. Those workers adduced satisfactory evidence to support the mass-balance prediction.

Data are summarised in Appendix 1 for the formation of hydrogen in the pyrolysis of butane in the acid-treated reactor. The yields of hydrogen calculated from the mass-balance were obtained by converting the differential yield of ethylene and ethane into an equivalent yield of

hydrogen. The yield of methane was common to both the determinations of hydrogen and of the C_2 hydrocarbons and was used to "tie" the results from the two chromatographs.

The calculated yields of hydrogen were generally about 50% higher than the observed values. A likely source of error in the analysis could be due to the following. The relative molar response factors which had been determined for hydrogen and methane on the C.E.C. chromatograph were dependent on the retention times of the components. With continued useage of the chromatograph, especially with only infrequent reconditioning of the column, the retention times would be considerably affected. The results tended to overrate the yield of methane given by the C.E.C. chromatograph and so to overrate the calculated yield of hydrogen. In the analysis of samples which contain traces of hydrogen there may also be some cumulative sampling errors which result from the high diffusivity of hydrogen.

The results from this study provide only a tentative endorsement of the hydrogen mass-balance expression. For more reliable and accurate results the chromatographic analysis would require some changes (Appendix 4).

A comparison of the product distributions reported by several workers.

In the region of the pyrolysis where the order of the reaction was 1.5 with respect to the butane, the following generalisations pertain to the product distribution:

1. The major products of the pyrolysis are methane, ethane, ethylene and propylene. Butenes accounted for about 1% of the total yield of cracked products. The yield of propane was negligible.

2. The yields of methane and propylene were identical within experimental limits of error.

3. The ethylene/ethane ratio was always greater than unity and increased with increasing temperature and decreasing pressure.

4. The proportion of C_2 hydrocarbons was independent of pressure (Series 6).

5. The product distribution did not change with increase in the contact time. The accompanying Table summarises data from Series 6 and 13.

Other recent workers (10,19,22) have agreed with the above generalisations. Quantitative comparison of product distributions is difficult because of the widely varying conditions under which the pyrolysis has been performed.

The proportions of methane and propylene are not too sensitive to the temperature and pressure and together account for about 70% of the total products:

Summary table of the product compositions at various contact times.

Series 6, Run No.	$\bar{\tau}$ sec.	%CH_4	%C_2H_6	%C_2H_4	%C_3H_6	CH_4/C_3H_6	Σ
32a	0.95	35.1	12.1	19.6	33.8	1.04	1.65
33	1.89	34.2	12.7	19.1	34.0	1.01	2.86
33b	1.94	34.3	12.7	19.2	33.8	1.02	3.00
34	3.66	34.5	12.1	19.3	34.2	1.01	4.88
34b	3.85	34.0	11.5	19.3	35.3	0.96	5.85
35	5.93	34.5	11.8	19.3	34.4	1.00	7.55
35a	5.88	34.4	11.2	19.1	35.4	0.97	7.50
Series 13							
1	0.58	35.4	12.0	19.3	33.6	1.05	0.81
1a	0.58	34.9	12.0	19.4	33.9	1.03	0.81
2	0.76	35.1	11.5	19.5	34.1	1.03	1.09
3	1.33	34.8	12.3	19.1	34.8	1.00	1.67
3a	1.38	34.5	12.0	19.0	34.4	1.00	1.68
4	2.20	33.8	11.6	19.1	35.6	0.95	2.50
4a	2.16	33.2	11.5	18.7	34.6	0.96	2.47
5	4.04	34.2	11.7	18.6	35.4	0.97	3.87
5a	3.96	34.0	11.5	18.8	35.5	0.96	3.90

This study: (Series 13, T = 570°C., p = 6.5 psia.
Runs 1 to 5a) Mean %age CH_4 = 34.5

Wang (27): (Table XI, T = 560°C., p = 14.7 psia.)
Mean %age CH_4 = 36.3

Sagert-Laidler: (Table III, T = 570°C., p = 202 mm.
Mean %age CH_4 = 32.3

Purnell-Quinn: (calculated from their expression for β) Mean %age CH_4 = 35.8

The results of Series 6 showed a generally satisfactory agreement with the results of Purnell and Quinn for several of the parameters associated with the product distribution, viz. the activation energies associated with the groups (α - 1) and β , and also the pressure dependence of the group (α - 1)p.

Sagert and Laidler gave a value of α as 1.91 at 570°C. and 202 mm.; the value of α estimated from Figure 9 is 1.95. Wang gave a value of α as 1.47 at 560°C. and 1 atm.; Figure 9 would give α = 1.30 under the same conditions.

In conclusion, the product distributions in the various studies are in good agreement - in contrast with the rate studies where overall rates differed by a factor of about 5. It is safe to conclude that the main propagation reactions were not significantly affected by the differing conditions under which the pyrolyses were performed.

The mechanism of the pyrolysis of n-butane.

Rice originally proposed that the major products of reaction were formed by the following propagation steps:

$$C_4H_9^{\cdot} \longrightarrow C_2H_4 + C_2H_5^{\cdot}$$

$$C_4H_9^{\cdot} \longrightarrow C_3H_6 + CH_3^{\cdot}$$

$$C_2H_5^{\cdot} + C_4H_{10} \longrightarrow C_2H_6 + C_4H_9^{\cdot}$$

$$CH_3^{\cdot} + C_4H_{10} \longrightarrow C_4H_9^{\cdot} + CH_4$$

and also the reactions:

$$C_2H_5^{\cdot} \longrightarrow C_2H_4 + H^{\cdot}$$

$$H^{\cdot} + C_4H_{10} \longrightarrow C_4H_9^{\cdot} + H_2$$

would increase the ethylene/ethane ratio above unity.

Later workers have generally adopted the above basic framework. Wang (27) took into account some of the guidlines given in Steacie's monograph (34). Wang's scheme included reactions of the propyl radical and also the formation of $H^{\cdot}$ from the butyl radical. Recent work on the propyl and butyl radicals which is discussed in an appendix (No. 2) shows that some of the reactions included by Wang are relatively slow and of little significance in influencing the product distribution.

Initiation of the pyrolysis is almost certainly due to a C-C cleavage (19):

$$C_4H_{10} \longrightarrow C_2H_5^{\cdot} + C_2H_5^{\cdot}$$

$$\longrightarrow C_3H_7^{\cdot} + CH_3^{\cdot}$$

Although all the free radicals involved in the pyrolysis are capable of contibuting to the termination of chains (27) only those radicals which are present in significant concentrations will contribute to the termination. Purnell and Quinn (19) presented an ingenious explanation as to why disproportion and recombination of ethyl radicals were mainly responsible for the termination of the pyrolysis. Their explanation invoked the observation that of the major products only ethane had an activation energy which was independent of the pressure (19). Sagert and Laidler used the rules for the overall order of the reaction developed by Goldfinger et al (4) to show that termination by ethyl radicals was dominant.

With the good agreement between the various studies of the product distribution a satisfactory account of the significant reactions involved in the initial stages of the pyrolysis should be possible. The following mechanism is proposed:

$$C_4H_{10} \longrightarrow C_3H_7^{\cdot} + CH_3^{\cdot} \qquad 1b.$$

$$C_4H_{10} \longrightarrow 2\ C_2H_5^{\cdot} \qquad 1c.$$

$$C_4H_9^{\cdot} \longrightarrow C_2H_4 + C_2H_5^{\cdot} \qquad 2.$$

$$C_4H_9^{\cdot} \longrightarrow C_3H_6 + CH_3^{\cdot} \qquad 3.$$

$$C_2H_5^{\cdot} + C_4H_{10} \longrightarrow C_2H_6 + C_4H_9^{\cdot} \qquad 4.$$

$$CH_3^{\cdot} + C_4H_{10} \longrightarrow CH_4 + C_4H_9^{\cdot} \qquad 5.$$

$$H^{\cdot} + C_4H_{10} \longrightarrow H_2 + C_4H_9^{\cdot} \qquad 6.$$

$$C_2H_5^{\cdot} \longrightarrow H^{\cdot} + C_2H_4 \qquad 7.$$

$$2\ C_2H_5^{\cdot} \longrightarrow C_4H_{10} \qquad 8a.$$

$$\longrightarrow C_2H_4 + C_2H_6 \qquad 8b.$$

$$C_3H_7^{\cdot} \longrightarrow C_2H_4 + CH_3^{\cdot} \qquad 9.$$

$$C_3H_7^{\cdot} \longrightarrow C_3H_6 + H^{\cdot} \qquad 10.$$

The above mechanism is essentially that proposed by Purnell and Quinn (19) with the additional reactions 9 and 10 to account for the fate of the propyl radical. The mechanism does not distinguish between the isomeric butyl radicals. With high conversion levels there are undoubtedly some secondary reactions; the above mechanism gives a good account of the initial stages of the pyrolysis.

Further comments based on the steady-state solution of the above mechanism are presented in Appendix 2.

A DISCUSSION OF THE "BREAK-OFF" PHEMOMENON.

Because the "break-off" phenomenon was unique to this study several postulates can be put forward to explain the effect. No single postulate however can be shown to unambiguously account for all the features of the effect. The three postulates are (1) a surface effect, (2) an effect due to preheating of the butane feed, (3) an effect which results from the decomposition of the ethyl radical.

1. A surface effect.

It is tempting to ascribe the effect to some surface contribution because no similar effect has been observed in quartz or pyrex reactors. The high surface-to-volume ratio of the microreactor and the low pressures of the butane would tend to promote a surface effect. The surface effects reported by Sagert and Laidler and by Purnell and Quinn were inhibitory effects in which quartz surfaces were considered to be capable of removing hydrogen atoms at the wall. In the gold reactor, a slight increase in the propylene/methane ratio was common to both the "break-off" region and to those runs (Nos. 93 to 95b, Series 11) wherein a carbonaceous deposit was apparently affecting the reaction.

Two further considerations are relevant. Firstly, on the basis of surface effects alone, it would be difficult to account for the finding that the overall rate of pyrol-

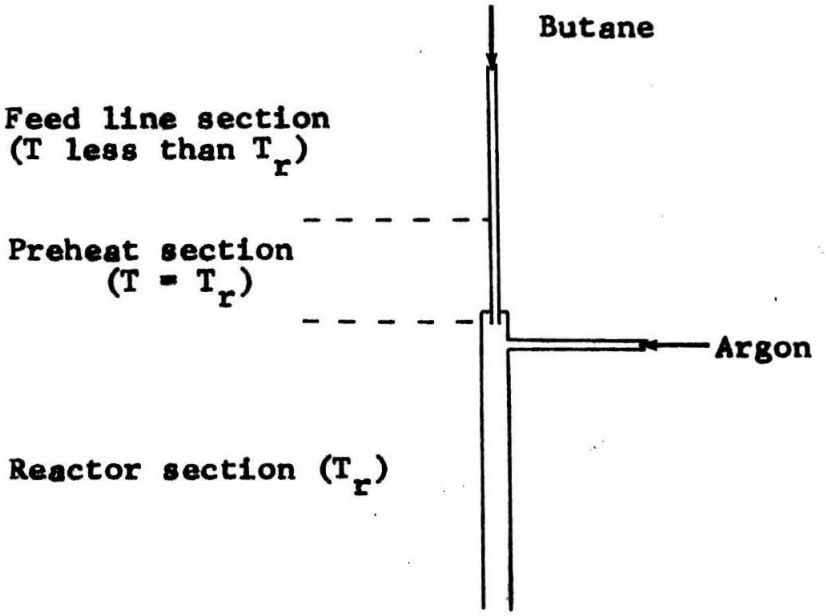
ysis was independent of the flowrate of gas through the reactor. Secondly, the data could be interpreted as showing that the "break-off" effect was not markedly influenced by changes in the surface-to-volume ratio or in the surface treatment. With the available data, the assumption of a surface contribution to the "break-off" effect would be plausible though untestable.

2. Preheating of the butane feed.

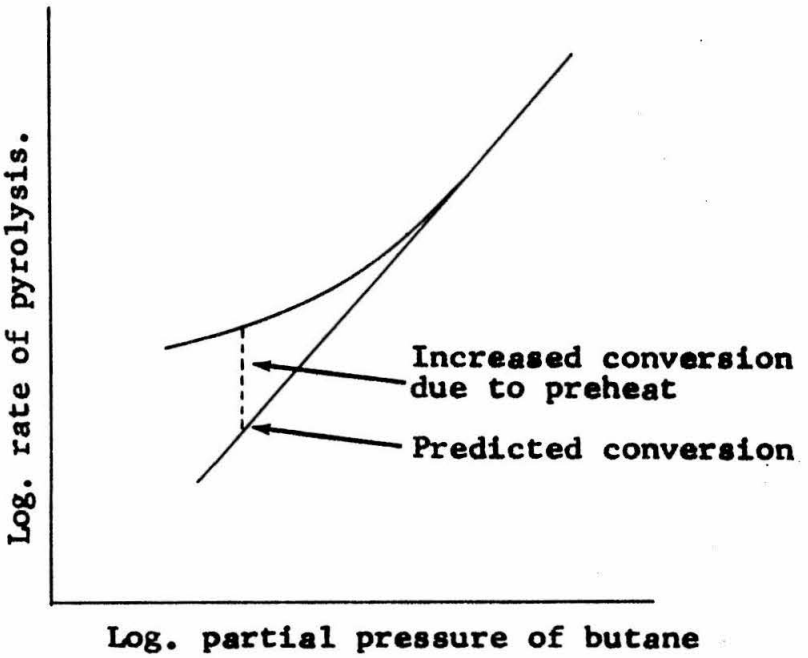
Under conditions of a low partial pressure of butane, the low flowrate of the butane would permit reaction of the butane in the inlet tube. Particularly in the all-gold reactor, the conduction of heat up the inlet tube would be sufficient to bring the temperature at the end of the tube almost upto the temperature of the reactor.

Consider the reactor as idealised in Figure 41. There is assumed to be a length x of the inlet tube in which the butane reacts at the total pressure of the reactor and at the mean temperature of the reactor. The butane is then diluted and reacts further in the main reactor tube. Figure 41 indicates the relative contributions to the overall conversion, which would then be erroneously calculated as a rate of pyrolysis in the reactor. The length x is to be calculated to account for the increased conversion.

Figure 42 is a copy of the data taken in Series 11;



Idealised model of the reactor with a preheat section.



Rate-pressure curve for a reactor with a preheat effect.

Figure 41.

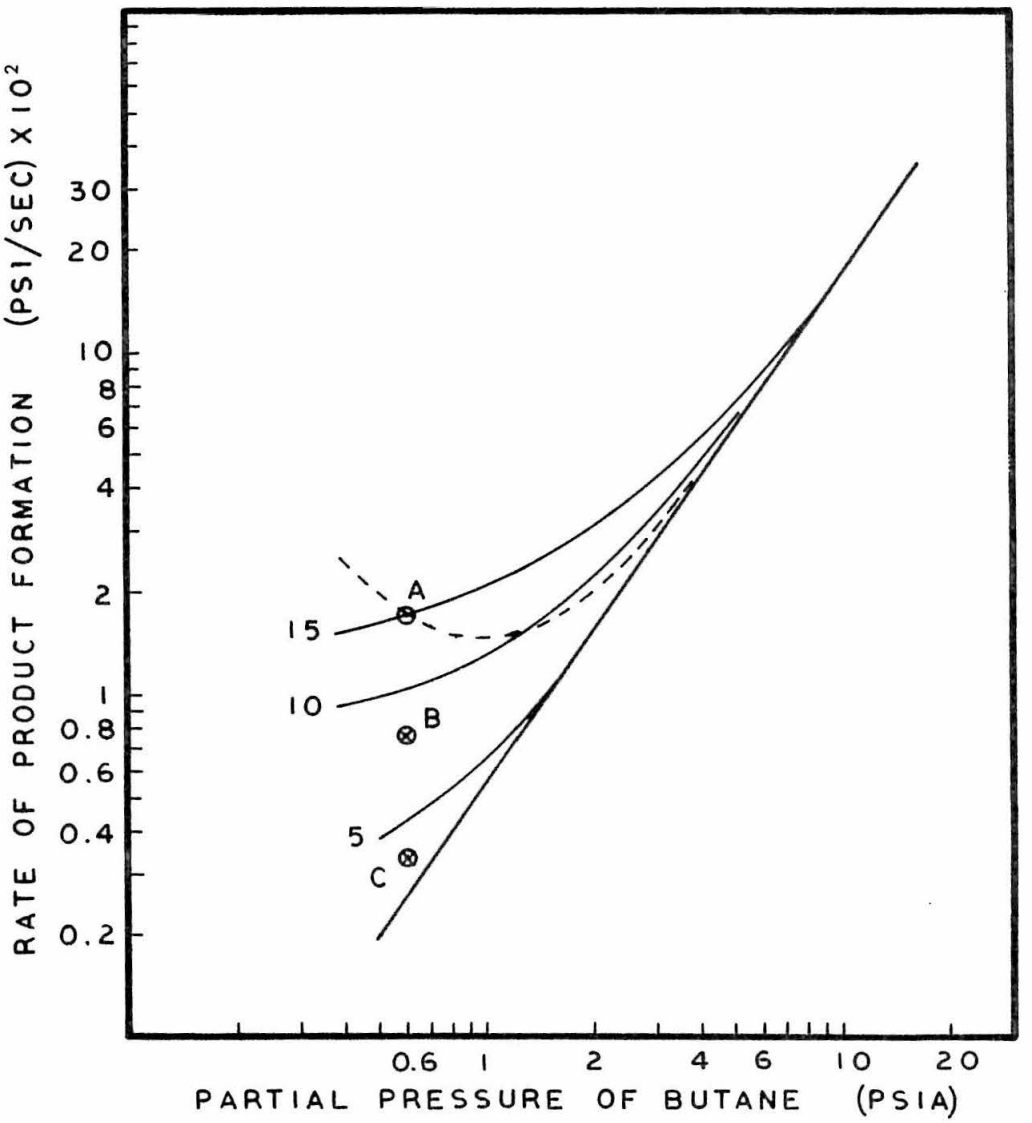


Figure 42. Rate-pressure curves in the region of the break-off effect. (Series 11)

the data in this Figure were all corrected to a mean contact time of 1.0 second. At point A on Figure 42 the conversion was 1.7×10^{-2} psia. whereas the conversion predicted by the 1.5-order relation would be 0.25×10^{-2} psia. Thus the increased conversion due to the preheat effect was $(1.7 - 0.25) \times 10^{-2} = 1.45 \times 10^{-2}$ psia.. Assuming this conversion in the preheater took place at a rate for p = 15 psia., i.e. 32×10^{-2} psi./sec. then the mean contact time in the preheat section was $1.45/32 = 0.045$ sec. The volume of the preheat section may be estimated from the contact time (0.045 sec.) and the flowrate of gas which was used to give the reactor conditions represented by point A (0.024 ml./sec.). With the inlet tubing diameter of 0.030 in. the length of the preheat section works out to be 0.24 cm.. This would be an entirely reasonable estimate for the length of the preheat section. In summary, when the pyrolysis is conducted at high dilutions, then even a short length of preheat section can have an enormous effect on the overall conversion.

It remains to be shown if the model can satisfactorily account for the variation of the rate in the "break-off" region with the total pressure and the partial pressure of butane. The model should also account for the variation of the ethylene/ethane ratio with the partial pressure. Referring to Figure 42 and taking point A as a basis for calculating the preheat effect (as above), the points B and

C were calculated for the total pressures of 10 and 5 psia. respectively. The dashed curve through point A represents a calculated isobar. The different flowrates of butane which are required to maintain the various partial pressures are reflected in the contribution of the preheat effect. Figure 42 indicates that the calculated preheat effect does not, by itself, give a completely satisfactory account of the "break-off" effect.

The preheat effect also makes a significant contribution to the variation in the ethylene/ethane ratio (α). The reaction in the preheat region gives rise to products which have a low value of α. Thus, the normal increase in α with decreasing pressure is offset by the fact that at lower partial pressures of the butane the reaction in the preheat tube becomes more significant. Figure 43 presents the experimental and calculated curves for the variation of α with the partial pressure; the agreement is quite satisfactory over the limited range of study.

In conclusion, the preheat model can account for some features of the "break-off" phenomenon; viz. the variation in the ethylene/ethane ratio and the independence of the effect on the type of diluent. The preheat effect could not entirely describe the rate-pressure curves. A simple calculation showed that the preheat effect could not account for the observation that the rate of pyrolysis did not depend

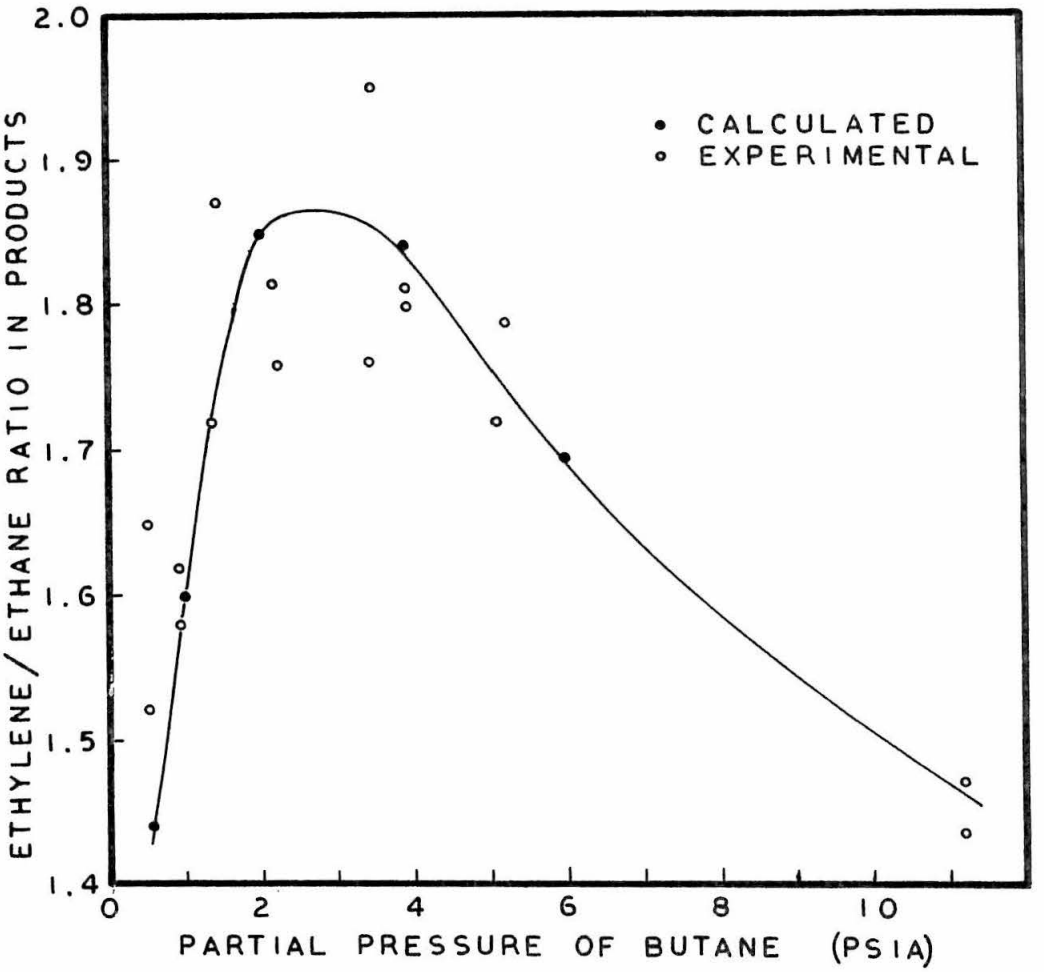


Figure 43. Calculated and experimental curves for the variation of the ethylene-to-ethane ratio with partial pressure of butane.

on the flowrate through the reactor. Whilst the preheat effect is highly plausible it cannot be entirely responsible for the "break-off" effect. An obvious experimental test of the preheat effect would be to add a fraction of the diluent to the butane feed so as to change the residence time in the preheat tube. The model discussed above is very unsophisticated. Allowance for effects such as the gradual heating-up of the butane stream could be made, but would probably exacerbate the difference between the experimental and calculated curves on Figure 42. For pyrolyses carried out at high dilution, the design of the inlet section should avoid localising undiluted gas at high temperatures.

3. Decomposition of the ethyl radical.

A further possible factor in the "break-off" effect is the effect of an added diluent on the decomposition of the ethyl radical:

$$C_2H_5^{\cdot} \longrightarrow C_2H_4 + H^{\cdot} \qquad (7)$$

This is a unimolecular reaction in its pressure dependent region (19). A steady-state treatment of the pyrolysis shows that a half-order term makes a significant contribution to the overall rate of pyrolysis (Appendix 2). This term is directly dependent on the rate of reaction 7 which in turn depends on the total pressure. Inert gases can be effective in collisional energy transfer from other free

radicals (71). The effect would be dependent on the type of inert gas, which would not be compatible with the results of Series 12. This postulate also could not explain the shape of the α - p curve.

Conclusion.

None of the three postulates can satisfactorily account for all of the features of the "break-off" effect. Much more experimental data will be required before the predominant factor is known. It would be preferable to check for a similar effect on the pyrolysis carried out in an entirely different reactor system, for example, a batch reactor.

CONCLUSIONS.

1. The pyrolysis of n-butane was found to be of 1.5-order with respect to the butane. The rate constant for the decomposition was given by:

$$k = 2.27 \times 10^{17} \exp(-66{,}000/RT) \quad \text{ml.}^{\frac{1}{2}}\ \text{mole}^{-\frac{1}{2}}\ \text{sec.}^{-1}$$

This expression was valid under the following conditions:

Temperature: 529 to 595°C.

Total pressure: 5 to 20 psia.

Mole fraction of butane: greater than 0.3, with various diluents.

Mean contact time: 0.55 upto 4.0 sec.

Conversion of n-butane: below 2%

Trace level of oxygen: below 2 ppm.

The above expression correlated data taken on an all-gold tubular reactor operated under conditions of laminar flow. The gold surfaces had been acid-washed and then conditioned by exposure to the pyrolysis.

2. With an excess of diluent in the system (argon, nitrogen, helium or carbon dioxide) a "break-off" effect was observed in which the rate of reaction was considerably increased over the rate predicted by the above expression. The increase in rate was directly related to the pressure of inert gas but did not depend on the type of diluent. The effect was also independent of the flowrate of gas

through the reactor. It was not possible to pinpoint the cause of the effect.

3. A comparison of the results of this study with the results of other recent workers (19,22,27) showed satisfactory agreement. The close correlations of the product distributions of the pyrolysis in the gold reactor and in a pyrex reactor showed that the main propagation reactions were homogeneous. However the rate of pyrolysis was markedly influenced by the presence of impurities on the surface of the gold. The exact composition of these impurities was not determined though the oxides of copper, iron and silver were probably present. There was also some indirect evidence of the formation of carbonaceous deposits.

4. The pyrolysis of n-butane was not sensitive to hydrocarbon impurities (except propylene) and was not affected by the presence of the diluent in the region of 1.5-order.

5. Trace amounts of oxygen were shown to markedly influence the formation of butenes and to exert a midly inhibitory effect on the formation of the cracked products. With higher levels of oxygen the evidence was that the butenes were the initial products of the reaction and that these were then rapidly attacked by oxygen.

RECOMMENDATIONS FOR FUTURE STUDY.

Several further areas of study could be undertaken using the equipment described in this work. In the pyrolysis of n-butane further studies are needed of the product composition at low pressures (below 50 mm.) to check the claims that the decomposition of the ethyl radical is a unimolecular reaction in its pressure dependent region (19). Accurate studies of the butene formation in the co-pyrolysis of n-butane and propylene should also be made. The cause of the "break-off" effect should be investigated and may suggest improvements in the design of the inlet section. In addition to a more systematic study of the partial oxidation of n-butane, many other reactions (both pyrolytic and oxidative) of hydrocarbons could be studied. Data on the pyrolytic decompositions of the higher paraffins are especially scarce.

Several minor modifications should be made to the equipment. Further efforts should be made to reduce the temperature gradients in the thermostat. A more reliable indication of the reactor temperature may be possible by using thermocouples with twisted elements ("Con-O-Twist"). Some minor modifications would be needed to operate the reactor in the "pulsed-flow" mode adopted by Keulemans (48). These modifications would allow start-up tests to be

carried out at very short intervals. Some of the changes which were proposed for the analytical equipment (Appendices 4 and 5) could also be effected.

Finally, a major long-term recommendation is that an all-gold batch reactor be used for studying the pyrolysis. A batch reactor would have several distinct advantages over the tubular flow reactor, particularly in terms of clarifying the role of the surfaces.

NOMENCLATURE.

A	constant in Arrhenius equation ($ml.^{\frac{1}{2}}\ mole^{-\frac{1}{2}}\ sec.^{-1}$)
F	total flowrate through the reactor (ml./min.)
k	rate constant for the decomposition in the region of 1.5-order ($ml.^{\frac{1}{2}}\ mole^{-\frac{1}{2}}\ sec.^{-1}$)
P	total pressure in reactor (psia.)
p	partial pressure of butane (psia.)
Q	flowrate of quench gas (ml./min.)
R_i	relative molar response for the component i on the flame-ionisation detector
S/V	surface-to-volume ratio of the reactor ($in.^{-1}$)
T	mean temperature of the reactor (°C. or °K.)
α	ethylene/ethane ratio in the cracked products
β	ratio of C_2 hydrocarbons to methane in products
$\bar{\tau}$	mean contact time (sec.)
Σ	sum of the relative moles of components in effluent
Σ_c	sum of the relative moles of components in effluent corrected to some arbitrary temperature, pressure and contact time

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APPENDIX 1.

Summary of data on the pyrolysis and partial oxidation of n-butane in a gold microreactor.

This appendix is a tabular summary of the data taken on the pyrolysis and partial oxidation of n-butane in the gold microreactors. The data are reported in chronological sequence. The tables are a condensed summary of the significant data taken in the course of the work. Data on the formation of the minor products in the pyrolysis are also included in a summary section.

Because data from the early series were not reproducible they are not included.

SERIES SIX.

Start-up test. Data on the pyrolysis as a function of running time after start-up.

Data corrected to temperature of 548.2°C.

Run. No.	Running time. (hrs.)	Butane pressure (psia.)	Contact time (sec.)	Moles product / Moles butane x 10^3 CH_4	C_2H_6	C_2H_4	C_3H_6	Σ_c
1	0.25	4.31	1.33	-	-	-	0.62	
2	0.50	4.37	1.33	0.68	0.24	0.36	0.68	1.96
3	0.75	4.40	1.32	0.60	0.20	0.31	0.69	1.70
4	1.00	4.46	1.32	0.68	0.24	0.36	0.69	2.02
5	2.00	4.46	1.32	0.74	0.26	0.39	0.74	2.06
6	15.5	4.38	1.33	0.82	0.28	0.43	0.80	2.10

The gold reactor with the stainless steel diluent line was used in the above runs. The reactor was 0.063 in. dia. by 11.6 in. long. Total pressure was 15.0 psia., the diluent was argon. Residual level of oxygen was below 2 ppm.. These conditions were maintained for the following set of runs which investigated the rate - pressure characteristics of the pyrolysis. Rates are recorded in units of psi./sec..

Data on the rate of pyrolysis with varying temperature and pressure. Runs 7 to 13a, Σ corrected to 550°C.

Run. No.	Temp. (°C.)	Butane pressure (psia.)	Contact time (sec.)	Σ x 10	Σ_c x 10	Rate. x 10^2	% C_2
7	548.0	7.47	0.96	2.28	2.65	2.00	31.1
7a	547.7	7.35	1.00	2.27	2.60	1.92	30.9
8	547.7	4.66	0.97	1.79	2.10	0.98	30.2
8a	547.5	4.65	0.96	1.68	2.05	0.96	30.4
9	549.5	3.28	1.05	1.78	1.75	0.575	29.8
10	549.0	1.39	1.02	1.04	1.10	0.155	29.8
10a	549.7	1.34	1.02	1.04	1.05	0.145	29.8
11	548.2	1.11	1.02	0.94	1.05	0.115	29.8
11a	547.8	1.06	1.02	0.94	1.05	0.113	30.8

Series 6 continued.

Run. No.	Temp. (°C.)	Butane pressure (psia.)	Contact time (sec.)	Σ x 10	Σ_c x 10	Rate x 10^2	% C_2
12	551.5	3.00	1.01	1.64	1.60	0.49	30.5
12b	550.5	3.02	1.01	1.61	1.60	0.48	30.4
13	551.7	0.96	1.03	1.07	0.96	0.092	30.9
13a	552.2	0.965	1.03	1.13	0.96	0.092	31.0
Runs 14 to 19; Σ corrected to 563.0°C., 1.0 sec..							
14	563.0	7.19	0.93	4.52	4.85	3.50	
14a	563.0	6.90	0.96	4.36	4.55	3.15	
15	562.7	3.27	0.97	3.06	3.15	1.03	
15a	562.7	3.23	0.965	2.82	2.95	0.96	
16	563.8	3.61	1.035	3.66	3.30	1.19	
16a	563.5	3.00	0.99	3.13	3.05	0.91	
17	562.2	1.93	1.04	2.52	2.50	0.485	
17a	561.7	1.91	1.02	2.47	2.60	0.495	
18	563.2	1.16	0.98	2.02	2.05	0.238	
18a	563.5	1.14	0.98	2.10	2.05	0.225	
19	563.4	7.80	0.96	5.13	5.10	3.95	
Runs 20 to 30a; Σ corrected to 575.0°C., 1.0 sec..							
20	575.0	7.60	0.93	8.22	8.80	6.69	
20a	575.2	7.61	0.93	8.18	8.70	6.60	
21	575.0	4.75	0.98	6.85	7.00	3.32	
21a	575.5	4.67	0.98	6.64	6.60	3.10	
22	575.2	2.78	0.93	5.29	5.60	1.55	
23	573.9	2.58	0.96	4.96	5.50	1.42	
23a	575.5	2.78	0.96	5.75	5.55	1.55	
24	575.7	1.88	0.98	4.76	4.55	0.86	
24a	574.7	1.80	0.99	4.68	4.80	0.87	
25	575.0	0.90	0.99	3.58	3.60	0.325	
25a	576.0	0.89	0.99	3.74	3.50	0.315	
26	575.0	0.755	0.98	3.54	3.60	0.272	
26a	573.7	0.75	0.98	3.29	3.60	0.270	
27	574.5	0.72	0.98	3.30	3.50	0.250	
27a	575.0	0.70	0.98	3.46	3.50	0.245	
28	573.5	0.61	0.99	3.34	3.65	0.225	
29	573.5	3.85	0.98	5.90	6.50	2.50	
30	575.6	3.94	0.97	6.62	6.60	2.60	
30a	576.0	3.90	0.96	6.08	6.00	2.45	
Run 31; Σ corrected to 592.0°C., 1.0 sec..							
31	592.0	3.98	0.97	12.9	13.4	5.33	
31a	591.8	3.92	0.97	12.4	12.9	5.05	

Series 6 continued.

Runs 32 to 35a; yield - time study; Σ corrected to 592.0°C., 7.50 psia.

Run. No.	Temp. (°C.)	Butane pressure (psia.)	Contact time (sec.)	Σ x 10	Σ_c x 10	$\%CH_4$	
32	592.0	7.70	0.94	15.8	15.7	34.8	1.60
32a	592.0	7.52	0.95	15.7	15.5	35.1	1.62
33	592.2	7.38	1.89	28.6	28.6	34.2	1.50
33b	591.8	7.25	1.94	27.9	30.0	34.3	1.51
34	592.5	7.56	3.66	50.4	48.8	34.5	1.60
34b	590.6	7.30	3.85	52.4	58.5	34.0	1.71
35	593.2	7.39	5.93	78.7	75.5	34.5	1.64
35a	592.7	7.14	5.88	7.40	75.0	34.4	1.70

Runs 36 to 40a; rate - pressure study; corrected to 592.0°C., 1.0 sec..

Run. No.	Temp. (°C.)	Butane pressure (psia.)	Contact time (sec.)	Σ x 10	Σ_c x 10	Rate x 10^2
36	592.7					
36	592.7	3.08	0.98	12.1	12.0	3.70
36a	591.5	3.12	0.96	11.2	11.9	3.71
37	591.0	2.16	1.00	9.58	10.1	2.19
37a	591.2	2.11	1.00	9.73	10.1	2.14
38	591.0	1.30	0.98	8.10	8.70	1.13
38a	589.6	1.27	0.98	7.66	8.70	1.10
38b	590.5	1.29	0.98	8.37	9.05	1.18
39	591.5	0.80	0.95	7.26	7.85	0.64
39a	591.5	0.81	0.96	7.48	8.00	0.65
40	592.2	1.11	0.96	8.12	8.35	0.92
40a	593.0	1.10	0.96	8.58	8.50	0.93

Run 41; Σ corrected to 563.0°C., 1.0 sec..

41	565.0	3.84	0.98	3.63	3.27	1.26
41a	566.0	3.92	0.98	4.31	3.58	1.40

Runs 42 and 43; Σ corrected to 536.0°C., 1.0 sec..

42	538.2	3.85	1.00	1.07	0.96	0.365
42a	536.2	4.01	0.99	0.95	0.98	0.385
43	534.7	7.64	1.01	1.26	1.36	1.02
43a	535.0	7.70	1.01	1.22	1.28	0.97

SERIES SEVEN.

Pyrolysis in the packed-tube gold reactor.

System: Gold reactor with stainless steel diluent line, reactor was 9.2 in. long, 0.0625 in. dia., packed with lengths of gold wire to give S/V ratio of 165 $in.^{-1}$
Total pressure: 15 psia. in all runs
Diluent gas: Argon
Oxygen level: below 2 ppm.

Data on the rate of pyrolysis at several temperatures and pressures of butane.

Runs 5 to 6a; Σ corrected to 553.0°C., 1.0 sec..

Run. No.	Temp. (°C.)	Butane pressure (psia.)	Contact time (sec.)	Σ x 10	Σ_c x 10	Rate x 10^2
5	550.2	11.3	0.98	2.84	3.25	3.65
5a	551.2	11.1	0.97	2.87	3.20	3.55
6	553.0	3.44	1.02	1.79	1.75	0.60
6a	553.2	3.38	1.01	1.79	1.75	0.59

Runs 8 to 9a; Σ corrected to 569.0°C., 1.0 sec.

8	568.5	3.17	0.99	3.36	3.50	1.10
8a	569.0	3.15	0.99	3.62	3.65	1.15
9	570.5	6.30	0.92	4.78	4.80	3.02
9a	570.5	6.30	0.92	4.74	4.75	3.00

Runs 10 to 11; Σ corrected to 587.0°C., 1.0 sec..

10	587.2	6.11	0.90	10.6	11.5	7.03
10a	587.5	6.05	0.95	10.3	10.8	6.55
11	588.5	3.51	0.98	8.47	8.15	2.85

Runs 12 to 19a; Σ corrected to 592.0°C., 1.0 sec..

12	593.2	3.66	0.92	10.9	11.0	4.03
12a	592.8	3.64	0.93	10.6	10.9	3.99
14	592.0	3.60	1.10	13.0	11.7	4.21
14a	592.0	3.35	1.05	11.6	11.0	3.70

Series 7 continued.

Run. No.	Temp. (°C.)	Butane pressure (psia.)	Contact time (sec.)	Σ x 10	Σ_c x 10	Rate x 10^2
14b	593.0	3.75	1.03	13.0	11.8	4.44
14c	591.5	3.66	1.02	11.4	11.5	4.20
15	591.2	7.10	0.94	15.9	17.5	12.4
15a	590.5	6.52	0.91	12.5	14.5	9.55
15b	590.7	5.93	0.96	13.1	14.2	8.45
16	591.7	4.65	0.96	12.5	13.1	6.05
16a	591.3	4.61	0.96	11.4	12.2	5.67
17	591.3	2.24	0.98	9.00	9.50	2.13
17a	591.3	1.77	1.01	8.47	8.70	1.53
17b	592.2	2.19	0.98	9.57	9.70	2.12
18	591.5	1.18	0.98	7.52	7.90	0.93
18a	591.5	1.20	0.98	7.51	7.90	0.95
19	590.7	0.92	1.01	7.66	7.90	0.73
19a	590.2	0.97	1.01	7.13	7.90	0.77
Runs 20 to 23b; yield - time studies, Σ corrected to 592.0°C.						
20	592.2	7.56	0.71	11.9	11.6	
20a	593.5	7.46	0.70	11.8	11.4	
21	592.7	7.48	0.93	15.6	15.0	
21a	593.0	7.46	0.94	15.0	14.3	
22	593.0	7.25	1.49	22.5	22.4	
22b	591.0	7.25	1.43	20.6	21.6	
23a	591.7	7.19	2.55	33.7	36.5	
23b	591.2	7.25	2.61	36.0	38.6	

SERIES EIGHT.

Partial oxidation in the packed-tube gold reactor.

System: Gold reactor with a stainless steel diluent line, this was tne same reactor used in Series 7.
Total pressure 15.0 psia., argon diluent.

Data on the variation in product composition with contact time, with 1.2% oxygen in the diluent. Data are corrected to p = 6.50 psia., T = 566.2°C.

Run. (No.)	Contact time (sec.)	(Moles product/mole butane in effluent) x 10^2							
		CH_4	C_2H_6	C_2H_4	C_3H_6	1-C_4H_8	t-C_4H_8	c-C_4H_8	1,3-C_4H_6
54	0.40	0.084	0.013	0.124	0.096	0.525	0.308	0.198	0.171
54a	0.41	0.081	0.013	0.116	0.095	0.536	0.309	0.190	0.161
55	0.54	0.097	0.016	0.136	0.102	0.410	0.242	0.167	0.119
55a	0.55	0.099	0.016	0.145	0.111	0.455	0.276	0.187	0.140
56	1.03	0.155	0.027	0.185	0.173	0.434	0.267	0.174	0.128
56a	1.08	0.164	0.029	0.189	0.178	0.506	0.273	0.180	0.153
57	1.02	0.164	0.026	0.158	0.148	0.460	0.270	0.178	0.152
57a	0.98	0.158	0.029	0.174	0.164	0.473	0.281	0.185	0.158
58	1.40	0.214	0.047	0.214	0.214	0.438	0.248	0.176	0.140
58a	1.37	0.212	0.046	0.232	0.232	0.473	0.277	0.167	0.142
Runs 64 to 66; data corrected to p = 6.50 psia., T = 522°C., (1.2% oxygen in diluent).									
64	0.91	0.011	0.0015	0.028	0.018	0.371	0.234	0.154	0.151
65	1.75	0.020	0.003	0.044	0.030	0.361	0.228	0.143	0.151
66	0.41	0.007	0.001	0.021	0.014	0.298	0.187	0.122	0.098

Series 8 continued.

Runs 67 to 72a; data corrected to T = 503°C., p = 6.50 psia., with 1.2% oxygen in diluent.

Run. (No.)	Contact time (sec.)	(Moles product/mole butane in effluent) x 10^2							
		CH_4	C_2H_6	C_2H_4	C_3H_6	1-C_4H_8	t-C_4H_8	c-C_4H_8	1,3-C_4H_6
67	1.14	0.003	negl.	0.012	0.0065	0.310	0.245	0.139	0.125
67a	1.20	0.003	negl.	0.012	0.0065	0.306	0.221	0.133	0.123
68	1.99	0.005	0.001	0.016	0.010	0.306	0.214	0.133	0.119
68a	2.00	0.005	0.001	0.014	0.009	0.314	0.234	0.124	0.118
69a	0.62	0.003	negl.	0.010	0.006	0.247	0.188	0.114	0.088
70	0.65	0.003	negl.	0.010	0.007	0.292	0.210	0.126	0.095
70a	0.65	0.003	negl.	0.011	0.007	0.280	0.198	0.115	0.087
71	0.52	0.002	negl.	0.008	0.0055	0.240	0.175	0.102	0.077
71a	0.52	0.0015	negl.	0.008	0.0055	0.238	0.170	0.101	0.078
72	0.425	0.0015	negl.	0.007	0.005	0.225	0.157	0.092	0.058
72a	0.42	0.0015	negl.	0.007	0.0045	0.212	0.149	0.087	0.060

Runs 73 to 77a; data corrected to T = 477°C., p = 6.50 psia., with 1.2% oxygen in diluent.

73	1.17					0.238	0.202	0.114	0.078
73a	1.30					0.261	0.203	0.113	0.085
74	0.75					0.193	0.154	0.085	0.059
74a	0.745					0.200	0.152	0.084	0.058
75	0.595					0.170	0.135	0.073	0.044
76	0.705					0.190	0.154	0.087	0.054
77a	0.445					0.145	0.117	0.063	0.037

Series 8 continued.

Runs 78 to 83; data corrected to T = 459.5°C., p = 6.5 psia. with 1.2% oxygen in diluent.

Run. (No.)	Contact time (sec.)	%Moles product/mole butane in effluent $1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$c\text{-}C_4H_8$	$1,3\text{-}C_4H_6$	$(O_2)_o$
78	1.16	0.194	0.150	0.080	0.048	4.45
78a	1.14	0.204	0.155	0.077	0.044	4.9
79	0.85	0.176	0.135	0.069	0.040	8.5
79a	0.90	0.178	0.140	0.071	0.041	7.4
80	0.70	0.159	0.119	0.062	0.033	9.1
80a	0.70	0.157	0.122	0.062	0.036	9.2
81	1.55	0.200	0.174	0.086	0.051	2.0
81a	1.57	0.190	0.165	0.085	0.048	1.75
82	0.53	0.111	0.095	0.051	0.028	10.6
82a	0.53	0.111	0.095	0.051	0.026	10.7
83	0.49	0.112	0.096	0.050	0.023	11.0

Runs 84 to 87a; data corrected to T = 445°C., p = 6.5 psia. with 1.2% oxygen in diluent.

84	1.90	0.156	0.147	0.072	0.038	3.3
84a	1.90	0.147	0.140	0.076	0.042	3.2
84b	1.91	0.154	0.144	0.070	0.038	-
85	1.47	0.130	0.128	0.061	0.033	5.4
85b	1.50	0.130	0.125	0.065	0.034	5.2
86	1.17	0.130	0.120	0.062	0.031	8.1
86b	1.18	0.130	0.122	0.063	0.032	7.6
87a	0.63	0.095	0.084	0.041	0.018	11.1

Runs 88 to 95b; data corrected to 445°C., 6.5 psia., with 4.0% oxygen in the diluent.

88	1.00	0.097	0.120	0.058	0.026	6.35
89	1.26	0.111	0.129	0.060	0.028	6.10
89a	1.26	0.118	0.123	0.061	0.030	6.14
89b	1.26	0.113	0.122	0.059	0.028	6.14
90	2.45	0.123	0.170	0.076	0.040	4.76
90a	2.42	0.147	0.177	0.077	0.041	4.78
90b	2.42	0.136	0.169	0.076	0.043	4.75
91	1.77	0.133	0.154	0.070	0.036	5.50
92	2.08	0.134	0.161	0.081	0.042	5.35
92a	2.08	0.134	0.157	0.072	0.038	5.15

Series 8 continued.

Run. (No.)	Contact time (sec.)	% Moles product/mole butane in effluent $1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$c\text{-}C_4H_8$	$1,3\text{-}C_4H_6$	$(O_2)_o$
93	0.94	0.100	0.110	0.052	0.024	6.40
93b	0.88	0.098	0.110	0.055	0.026	6.40
94	1.39	0.108	0.136	0.068	0.034	6.00
95	0.49	0.085	0.093	0.041	0.016	6.75
95a	0.51	0.092	0.094	0.044	0.019	6.80
95b	0.51	0.092	0.092	0.044	0.017	6.75
Runs 96 to 107; with 4.0% oxygen in diluent, data corrected to T = 459.5°C., p = 6.50 psia..						
96	1.53	0.183	0.191	0.095	0.053	5.33
96a	1.59	0.173	0.183	0.092	0.055	5.20
96b	1.59	0.191	0.191	0.092	0.051	5.20
97	1.56	0.160	0.176	0.093	0.053	5.20
97a	1.58	0.152	0.169	0.086	0.054	5.20
98	2.32	0.228	0.253	0.114	0.062	3.90
98a	2.34	0.216	0.246	0.120	0.065	3.90
98b	2.33	0.191	0.234	0.110	0.064	3.95
99	1.89	0.204	0.214	0.104	0.064	4.70
99a	1.87	0.207	0.216	0.106	0.060	4.70
99b	1.88	0.199	0.203	0.102	0.063	4.70
100	0.72	0.145	0.138	0.069	0.035	6.35
101	0.77	0.138	0.139	0.070	0.038	6.30
101a	0.77	0.136	0.133	0.075	0.040	6.30
101b	0.76	0.142	0.144	0.068	0.037	6.30
102	0.735	0.140	0.125	0.068	0.035	6.35
102a	0.74	0.143	0.137	0.070	0.038	6.35
103	0.505	0.125	0.115	0.058	0.027	6.80
103a	0.515	0.116	0.107	0.059	0.030	6.80
104	0.42	0.115	0.107	0.049	0.022	6.80
104a	0.42	0.110	0.102	0.052	0.024	6.90
105	0.425	0.108	0.099	0.050	0.021	6.90
105a	0.425	0.108	0.099	0.048	0.023	6.90
106	0.785	0.147	0.142	0.072	0.038	-
107	1.09	0.169	0.165	0.086	0.044	6.00

Series 8 continued.

Runs 110a to 118b; with 4.0% oxygen in diluent, data corrected to T = 477°C., p = 6.50 psia..

Run. (No.)	Contact time (sec.)	% Moles product/mole butane in effluent. $1\text{-}C_4H_8$	$t\text{-}C_4H_8$	$c\text{-}C_4H_8$	$1,3\text{-}C_4H_6$	$(O_2)_o$
110a	2.95	0.258	0.292	0.148	0.122	-
111a	1.78	0.246	0.254	0.136	0.101	2.94
112	1.54	0.209	0.228	0.122	0.088	3.91
112b	1.56	0.231	0.237	0.126	0.083	3.96
113	1.23	0.218	0.218	0.115	0.083	4.85
113a	1.23	0.211	0.209	0.115	0.081	4.85
114	0.92	0.192	0.176	0.098	0.069	5.70
114a	0.92	0.188	0.176	0.097	0.069	5.70
115	1.05	0.220	0.202	0.112	0.074	5.35
115a	1.02	0.206	0.193	0.110	0.076	5.35
116a	0.81	0.189	0.176	0.098	0.067	5.85
117	0.655	0.179	0.152	0.088	0.055	6.20
117a	0.655	0.175	0.154	0.088	0.055	6.10
117b	0.655	0.174	0.149	0.084	0.056	6.15
118	0.415	0.145	0.127	0.072	0.040	6.70
118a	0.415	0.145	0.126	0.072	0.040	6.65
118b	0.415	0.146	0.120	0.070	0.038	6.70

Runs 119 to 122; with 4.0% oxygen in diluent, data corrected to T = 503°C., p = 6.50 psia..

119	0.72	-	0.250	0.148	0.132	-
119a	0.715	0.314	0.220	0.129	0.121	4.80
119b	0.695	0.310	0.229	0.136	0.122	4.90
120	0.50	0.267	0.206	0.115	0.097	5.80
120a	0.50	0.254	0.188	0.106	0.095	5.75
120b	0.495	0.236	0.184	0.103	0.094	5.85
121	0.395	0.208	0.162	0.094	0.078	6.25
121a	0.405	0.206	0.164	0.099	0.081	6.10
122	1.28	0.367	0.314	0.165	0.153	2.25

Series 8 continued.
Runs 125 to 131b; with 4.0% oxygen in diluent, data corrected to T = 566°C., p = 6.50 psia..

Run. (No.)	Contact time (sec.)	(Moles product/mole butane) in effluent x 10^2							
		CH_4	C_2H_6	C_2H_4	C_3H_6	1-C_4H_8	t-C_4H_8	c-C_4H_8	1,3-C_4H_6
125	1.88	0.086	0.020	0.187	0.119	0.771	0.490	0.298	0.354
125b	1.99	0.096	0.022	0.196	0.134	0.719	0.446	0.281	0.322
126a	1.53	0.088	0.018	0.173	0.116	0.717	0.452	0.272	0.316
126b	1.50	0.088	0.018	0.169	0.117	0.726	0.447	0.267	0.318
127	1.88	0.092	0.021	0.174	0.112	0.734	0.441	0.254	0.300
128	2.23	0.122	0.025	0.222	0.150	0.740	0.449	0.257	0.307
128a	2.22	0.122	0.028	0.206	0.143	0.693	0.416	0.246	0.286
129	1.31	0.104	0.020	0.184	0.126	0.755	0.454	0.265	0.313
130	0.58	0.056	0.007	0.139	0.082	0.790	0.506	0.269	0.316
130b	0.58	0.056	0.008	0.129	0.077	0.782	0.483	0.260	0.339
131	0.365	0.047	0.006	0.114	0.068	0.724	0.445	0.244	0.274
131b	0.365	0.043	0.005	0.112	0.068	0.727	0.419	0.236	0.270